

## PHOTOVOLTAICS: A REVIEW OF CELL AND MODULE TECHNOLOGIES

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**Abstract**—This review centers on the status, and future directions of the cell and module technologies, with emphasis on the research and development aspects. The framework is established with a consideration of the historical parameters of photovoltaics and each particular technology approach. The problems and strengths of the single-crystal, polycrystalline, and amorphous technologies are discussed, compared, and assessed. Single- and multiple-junction or tandem cell configurations are evaluated for performance, processing, and engineering criteria. Thin-film technologies are highlighted as emerging, low-cost options for terrestrial applications and markets. Discussions focus on the fundamental building block for the photovoltaic system, the solar cell, but important module developments and issues are cited. Future research and technology directions are examined, including issues that are considered important for the development of the specific materials, cell, and module approaches. Novel technologies and new research areas are surveyed as potential photovoltaic options of the future. © 1997 Published by Elsevier Science Ltd

Photovoltaics (PV) is a technology that has already demonstrated its effectiveness and holds great promise in electrical generation for the world. Its building-block versatility makes it suitable for large, central-station installations of multiple-MW proportions, as well as smaller and diverse rural-electrification applications of 100 W size for lighting and communications. It has proved its worth for water pumping and for consumer products. It is also an enabling technology, one that creates markets for other products in wireless telecommunications, transportation, data acquisition, space power, emergency and disaster relief, intelligence, and the environment. These end-use markets are perhaps the current growth areas for the technology because PV is attached intimately to technological products and services that are exploding in their own demand. In this respect, photovoltaics has a leveraging effect in many commodities measured by discounted cash flow. The technology, however, does not yet have an established and commanding position in these world markets. To an extent, the PV products are proven, but they require attention in many phases—including R&D—to become competitive. This review is directed toward the building blocks of the photovoltaic system—the solar cell and module—with the intention of providing the reader with some gauge of where the technology has been, where it is, and where it is directed for these components. This is an extensive technical look at photovoltaics that provides insights to the current trends, the problems, and the opportunities for development.

It is based on the understanding and premise that the performance and economics of these photovoltaic building blocks help guide the viability and acceptance of the technology among the world's energy-generation alternatives.

### 1. INTRODUCTION AND HISTORICAL PERSPECTIVES

Certainly a great deal of technical progress in photovoltaics (PV) toward a conventional energy source status has been made since the 1960s. However, PV has been a research and development entity for more than a century and a half. A histogram representing the volume publications dealing with photovoltaics from the early years to the present time is presented in Fig. 1. The current solar cells are a realization and utilization of the fun-

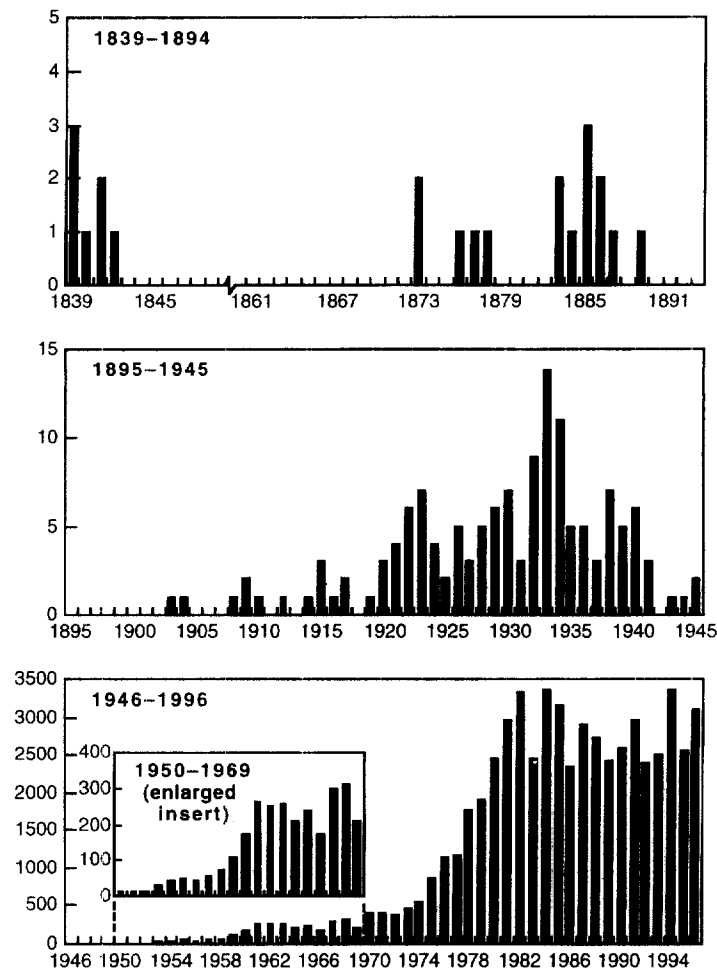


Fig. 1. Histogram of publications dealing with photovoltaics from 1839 until the present time. [Note: this histogram is assembled from a number of databases. Electronic compilations are only available from 1974. Earlier data have been gained from examination of abstracts, related journals, and other published material. It should be understood that these data are a represent best estimates to the volume of photovoltaic publications.]

damental physical phenomena first observed in the early 19th century. In 1839, Edmond Becquerel was involved in a series of experiments studying electricity, the subject of intense research interest in those times [1, 2]. His work centered on the behavior of solids in electrolytes. He observed that when metal plates (platinum or silver) immersed in a suitable solution were exposed to light, a small voltage and current were produced—the photovoltaic effect. Little more was recorded until 1878 when Adams and Day [3], following the work of Smith [4] on photoconductivity in elemental selenium, published the first report directly attributed to the photovoltaic effect in a solid. The potential of this energy source was touted five years later by Fritts [5], who not only fabricated the first thin-selenium solar cells, but also forecast their use as large-scale, low-cost electrical generators (alternative to fossil-fuel sources). However, Fritts' experiments and speculations were met with scepticism by some scientific colleagues who were still limited in their evaluation by the constraints of classical physics. Although these light-sensitive devices functioned and the experiments could be reproduced, the mechanisms could not be explained thoroughly until the advent of quantum mechanics. In the 1930s and 1940s, research on a host of materials, including selenium [6, 7], cuprous oxide [8–13], lead sulfide [14], and thallium sulfide [16], continued. Interestingly, in the period 1930–1933, L. Grohndahl provided pioneering results with more than 30 publications on cuprous oxide/copper solar cells [17]—a technology that was resurrected in the 1970s because of its economic promise. In the early 1940s, two short reviews entitled “The Photovoltaic Effect” were published by Adler [16] and Cassel [18]. In 1941, a primitive silicon photovoltaic device was patented by Ohl [19], who produced the cell by impurity variation during crystal growth. The laboratory device had a conversion efficiency substantially below 1% and a limited operating lifetime. Ohl's discoveries are more noted for identification of “negative and positive” Si, rather than the photovoltaic device itself. These embryonic solar cells were more curiosities than serious electronic components, although Ohl and colleagues continued work into the early 1950s with improvements in the quality of the Si and variations in processing devices [20]. It was in the mid 1950s, with the emergence of semiconductor rectifiers and transistors, that the solar cell first made an impact in the technology arena. Chapin, Fuller, and Pearson of Bell Telephone Laboratories developed the silicon solar cell [21], which was an outgrowth of an observation that the Bell Labs' diodes could generate a significant amount of current and voltage when exposed to light. This “solar battery” was more efficient (about 6% under the irradiance conditions used) than any previous cell. Its impact was immediate, and within a year, two commercial solar-cell companies established production facilities. Less cited are the RCA “electron-voltaic” cells (both Si and Ge), which were published by Rappaport [22] 5 months before the Bell Labs' result. The early laboratory work on this device was toward sunlight operation, but the work was redirected to more intense radiation sources because it was thought that the solar resource was too diffuse. However, this work clearly laid the foundation for the importance of the semiconductor's bandgap on performance. It is sometimes overlooked that almost coincident with the publication of the Si solar cells was the report in 1954 by Reynolds *et al.* [23] of the first cuprous sulfide/cadmium sulfide heterojunction—which served as the beginning and impetus for an intense effort in thin-film photovoltaics.

Since the 1950s, PV has developed rapidly. Small-scale use, such as telephone repeaters requiring 10s of watts, were typical early markets [24–26]. The first real impacts were realized for space applications. Through the persistence of a small group of scientists and engineers working on the first U.S. space satellites [27], permission was granted to provide

back-up power on Vanguard I in 1958. The small, 6-Si cell panel, configured so as not to interfere with the working of the satellite, provided about 5 mW of power. When the batteries ceased operation after a few months, this PV power source continued to operate the transmitter over the six-year life of the satellite. This humble beginning not only established some reliability benchmark for the technology, but marked the start of an industry—one that has grown from the sub-watt level for extraterrestrial power sources to current manufacturing lines exceeding 10 MW per year capacities for terrestrial needs [28]. Limitations in fossil-fuel resources, the political instabilities in the Middle East, and the oil embargo in the mid 1970s turned the industry to address and support these terrestrial requirements. Government programs in the U.S., Europe, and the Far East were initiated in response to these needs [29]. The technology progressed, but the urgency associated with oil and gas shortages subsided in the 1980s. Instead, the environment (including pollution, global warming, greenhouse effect, etc.) and the social costs of fossil and nuclear sources continued to weigh the balance in favor of development of clean renewable and sustainable energy.

Over this period of terrestrial investment, the technology and industry developed extensively—indicated by module shipments exceeding 90 MW per year, and installed remote and central power stations producing hundreds of megawatts [30]. It is this recent time period, the technology status, and the perspectives and expectations that provide the framework by this review. The past 20 years have been highlighted by research into new materials, development of novel devices, engineering of new and more effective structures, improvements in processing, and augmentation and scale-up of the manufacturing sector. The extent of the earlier materials and device research is indicated by the compendium included in Appendix I. The evolution of the photovoltaics technology has been remarkable, but considerable research and development remain in order to make PV acceptable, widespread, and cost effective. Current problems with photovoltaics, the position of the technology, the material and devices under development, research needs, and the future are discussed herein. Many of the projections, objectives, and economic arguments are based upon the U.S. Department of Energy Five-Year Plan [30]. Numerous studies have been used to formulate and validate this plan, and these numbers have been used to guide the research goals in this review. This plan mandates research into all photovoltaic options to continue to make the technology competitive on a wider scale. Although crystalline silicon remains the mainstay technology, the other options are expected to penetrate the markets as they become commercial realities. (It is acknowledged that external effects—many of which are difficult to quantify such as social costs, environmental and climatic effects of operation of energy plants, hidden subsidies, production of intermediate goods, etc.—add to the value of photovoltaics in comparison to other electricity generation approaches.)

This work is intended to be a comprehensive and critical treatment of photovoltaics, centering around cell and module R&D. For more details of the physics, materials properties, systems, and engineering aspects of PV, the reader is directed to Appendix II, a bibliography included at the end of this report. This review works logically through single-crystal, polycrystalline, and amorphous technologies, treating both bulk and thin-film approaches. Both flat-plate (one-sun) and concentrator cells are covered and compared. At the conclusion of each section, a statement of concerns, and issues with each of the technologies is included. These relate to research issues, as well as to those matters (manufacturing, applications, cost, and industry) that mold and formulate technology direction and investment.

## 2. PERFORMANCE

In this review, cells and modules are compared for performance, including conversion efficiency, power generation, and related characteristics. The accurate and standardized determination and reporting of the performance of photovoltaic cells and modules are essential for advancing the technology. The validity of these evaluation tools and procedures needs to be established for meaningful comparisons of the cell, module, and array performance, not only between the various technologies, but also, to fairly and accurately evaluate alternative methods of electrical power generation. Assessing the performance of cells and modules under defined and accepted standard, reproducible test conditions is a major requirement for the worthwhile appraisal and eventual acceptance of photovoltaics. Because of this, performance evaluation is the most controversial and sensitive area of characterization. Efficiency has a straightforward definition, but its evaluation can be complex [31]. As photovoltaic devices and modules have become more complicated, so have the methods required to precisely evaluate their performances. This has been further emphasized with the establishment of the Photovoltaic Global Approval Programme (PV GAP), a worldwide industry-driven organization that promotes and maintains a set of standards and certification procedures for PV products and systems. More standards and regulations may cover this area of characterization than any other. There are certainly as many innovative methods used in attempting to circumvent these rules and procedures as the number of such rules and procedures themselves! Therefore, the determination of performance will be discussed and examined for the purpose of providing the basis for the numbers reported in this review.

The efficiency of a photovoltaic device is defined in terms of the power produced from the incident photon (sunlight) power [31]. The common approach is to obtain the light-generated current-voltage ( $I$ - $V$ ) characteristics and ascertain the maximum power point [31, 32].

Terrestrial cell and module measurements in the United States are traced to the publication of the *Solar Cell Radiation Handbook* by NASA and JPL in 1973 [33]. Although written for space applications, this document provided the foundation for instrumentation, sunlight measurements, relevant solar cell parameters, and important environmental conditions. Two important Terrestrial Photovoltaic Measurements Workshops were conducted in 1975 and 1976 under the auspices of the Energy Research and Development Administration (ERDA) and NASA Lewis Research Center. From these workshops, a set of consensus terrestrial cell and array measurement procedures were adapted [34], providing the U.S. terrestrial program with initial guidance for evaluating PV components. These procedures were influenced by the experiences with extraterrestrial PV—and they were refined over the next decade to better represent the terrestrial conditions. Over this time period, national and international intercomparisons, technique developments, establishment of international standard measurement laboratories, and international cooperations have led to a current set of standard measurement and reporting conditions and procedures, which have increased confidence in efficiency measurements worldwide [35–37]. (It should be noted that the world standards organization [ASTM, ANSI, IEEE, IEC, EUR, ISO] have worked with the photovoltaics industry and various government agencies to develop tests that are wider in scope than just those relating to efficiency or performance [38–43]. In most cases, these tests provide the industry with a set of criteria for product acceptance, and the consumer with a degree of confidence in the reliability of the product.)

Table 1. Standard measurement and reporting conditions for solar cells and modules

Application	Irradiance (W/m <sup>2</sup> )	Reference spectrum	Temperature (°C)
<i>Cells</i>			
Terrestrial	1000	Global	25
Terrestrial (concentrator)	> 1000	Direct	28
<i>Modules and arrays</i>			
Method 1	1000	Global	25
Method 2	1000	Global	NOCT
<i>Modules and systems</i>			
Terrestrial	1000	Prevailing	20 (ambient)
<i>Space</i>			
Extraterrestrial	1367	AM0	25, 28
1 astronomical earth-sun distance	(1353, 1372)		

NOCT: Normal operating cell temperature, defined as the temperature a module will attain with 20°C air temperature, 800 W/m<sup>2</sup> total irradiance, and a 1 m/s wind speed (ASTM Standard E1036).

### 2.1. Standard measurement conditions and measurement uncertainty

The standard measurement and reporting conditions are defined by reference to spectral irradiance, total irradiance, temperature, and standard definition of area—as summarized in Table 1 [31, 38]. World photovoltaic organizations continue to review and revise these. However, their examination provides some insight into the sources of error that can enter into the determination of the efficiency of a cell or module. Some origins of error or accuracy problems are included in Table 2 and relate to geometry (device area), electronic instrumentation (calibration, stability), light source (irradiance, spectral distribution, spectral measurement, uniformity, conditions), contacts, temperature, procedures, and others [44–49]. The best possible determination of efficiency (or related parameters) depends on the limits of measurement uncertainty [44, 45]. The total measurement uncertainty is usually expressed as

$$U = B + tS, \quad (1)$$

where  $B$  is the bias error,  $S$  is the random or precision error component, and  $t$  is the Student coefficient, which depends on the confidence level (typically 95% or 99%) [44, 45]. These parameters have been treated both analytically and experimentally, and a representative set of elemental errors relating to the primary performance-related cell and module parameters, and for instrumentation and techniques [31]. The most controlled environment (i.e. simulator-based measurements) provide the best accuracy. Typical methods are those commonly encountered in laboratory environments (i.e. not standards laboratories). These accuracy observations are based on intercomparisons of measurements between worldwide laboratories. The results of formal, international intercomparisons are also cited and provide similar accuracy ranges. In general, the confidence in measuring accurate and believable efficiencies has increased significantly worldwide owing to the efforts over the past 15 years of the standards and testing organizations.

### 2.2. Efficiency definitions and determination

All efficiency measurements are conducted according to the conditions posed in Table 1 [31, 38]. The major ingredients in the experimental approach are: (1) the device (cell or

Table 2. Several common sources of measurement uncertainty, including error bias and random or accuracy problems affecting the determination of performance of photovoltaic devices.

(a) Bias and random components for selected cell parameter measurements to illustrate the potential relative contribution of each to the efficiency determination (see Ref. [46])

Parameter	Bias $B$ (p.p.m.)	Random $R$ (p.p.m.)
Maximum power, $P_{\max}$	+2000 to -2800	2000
$I_{\text{R,R}}$	$\pm 11,200$	0
$I_{\text{R,S}}$	+7800 to -8600	1840
Area	$\pm 1000$	190
Spectral mismatch factor, $M$	$\pm 5400$	300
Efficiency	$\pm 16,000$	3400

The uncertainty limit can be defined as  $U = B + tR$ , where  $t$  is Student's confidence value (see Ref. [45]).

(b) Bias and random error percentages and total uncertainty for various calibration methods for total irradiance methods to compare the relative error associated with each approach

Calibration method	Total irradiance method/technique	Bias $B$ (%)	Random $R$ (%)	Total uncertainty (%)
Global fixed tilt	Pyranometer	3.1	1.5	4.3
Global fixed tilt	Direct + diffuse	2.3	1.2	3.2
Global normal	Pyranometer	2.5	1.5	3.7
Global normal	Direct + diffuse	0.8	1.2	2.5
Direct normal	Radiometer	0.5	0.3	0.7
Simulator	Reference	1.0	0.2	1.1
(Continuous X-25)				
Simulator	Reference cell	1.4	1.2	3.0
(pulsed SP1SUN)				
AM0 (balloon)	Not measured	0.5	0.2	0.7
AM0 (airplane)	Not measured	1.0	---	1.0

(c) Typical accuracies in the determination of efficiency for various cell and module measurements, including single-junction and multiple-junction devices

	Best methods (%)	Typical methods (%)	Intercomparisons† (%)
<i>Single junction</i>			
Cells (1 sun)	$\pm 2$	$\pm 5$	$\pm 5(\pm 3)^*$
Cells (concentrator)	$\pm 3$	$\pm 5$	
Modules	$\pm 3$	$\pm 5$	$\pm 7(\pm 3)^*$
<i>Multiple junction</i>			
Cells (1 sun)	$\pm 3$	$\pm 5$	
Cells (concentrator)	$\pm 4$	$\pm 8$	
Modules	$\pm 5$	$\pm 8$	

\* Single-crystal and multi-crystal silicon only.

† Based on PEP85 and PEP87.

module), (2) the environmental conditions (temperature), (3) the light source, and (4) procedures. The single-junction device is used as the focus for this section, and the complications imposed by multiple-junction cells and concentrators are indicated in the next section.

*Device.* The cell or module is a given parameter, but one that can impose severe uncertainty and error into the reported efficiency. Several sources of error relate to the device, with the major ones including contacting, illumination geometry, and area definition and measurement. For research devices, contacting and area determination can introduce error, especially if the cell area is less than 1 cm<sup>2</sup>. Probe shading and contact resistance are concerns. Four-point Kelvin contacts are preferred. A ragged circumference, insufficient isolation from the substrate (e.g. mesa structures), and reflections have greater influence on sub-cm<sup>2</sup> area cells. The photovoltaic community has adopted a strict total-area definition [50–53]:

Cell: The entire frontal area of the solar cell, including the cell grid [50].

Module: The entire frontal area of the module, including borders and frame [50].

For standard reporting, the *total area* of the cell, as defined above, is mandatory. Sometimes, an “active-area” definition is used for the laboratory research cell, but this definition has not been adopted by any world standards organization. This “active area” varies from report to report, but it basically considers the total area of the cell minus the grid area. It is used primarily for research purposes, to demonstrate the quality of the material. In the case of modules, an “aperture area” can be cited, which is defined as the total area minus the area of the frame and/or borders [54]. Other areas can be found in the literature, including those relating to other terms in the hierarchy such as panel, submodule, and array. However, the standards have been adopted and should be used for proper and fair comparisons among and between technologies. If other (non-standard) areas are used, the report should at least make sure that the area definition is clearly stated and should include the standard measurement condition, as well.

*Temperature.* The temperature is defined, in the formal sense, as the junction temperature of the device under test [31, 38]. This can be determined by knowing the device material (e.g. Si), but for more advanced cells having inhomogeneities, the analytical determination is difficult. In most cases, it is sufficient to measure the surface temperature of the device, heating only the back surface of the structure [55–59]. Superstrate structures (where frontal glass is exposed to the light source) and modules (which have large areas) pose obvious problems [57]. The normal operating-condition temperature (NOCT) is sometimes employed for modules [59]. However, because of the sensitivity of cell efficiency to temperature, it is essential to control this parameter for standard measurements— or at least to confine its uncertainty to known limits. It should also be emphasized that the *standard* temperature (e.g. 25 °C for cells) is only a reference. It certainly does not reflect the operating condition in some of the more severe climates required for photovoltaic systems, in which temperatures can exceed 60 °C. System design must match the system location, not a standard used for other purposes.

*Irradiance and spectrum.* Irradiance and spectrum are sensitive determinations for performance measurements. Simulators ensure reproducibility and control, and spectral distribution and uniformity are the most important gages. Simulators are classified with respect to these parameters, with three major simulator types [60]. For cells and modules, standards laboratories employ class A simulators which have the highest parameter constraints.



The standard spectra for space (termed air-mass zero or AM0) and terrestrial (AM1.5) or global conditions are shown in Fig. 2. The definition of air mass (AM) is depicted graphically in Fig. 3 and is the ratio of path length along the oblique trajectory to the path length in the zenith direction [61]. Essentially, AM0 means there is no atmosphere between

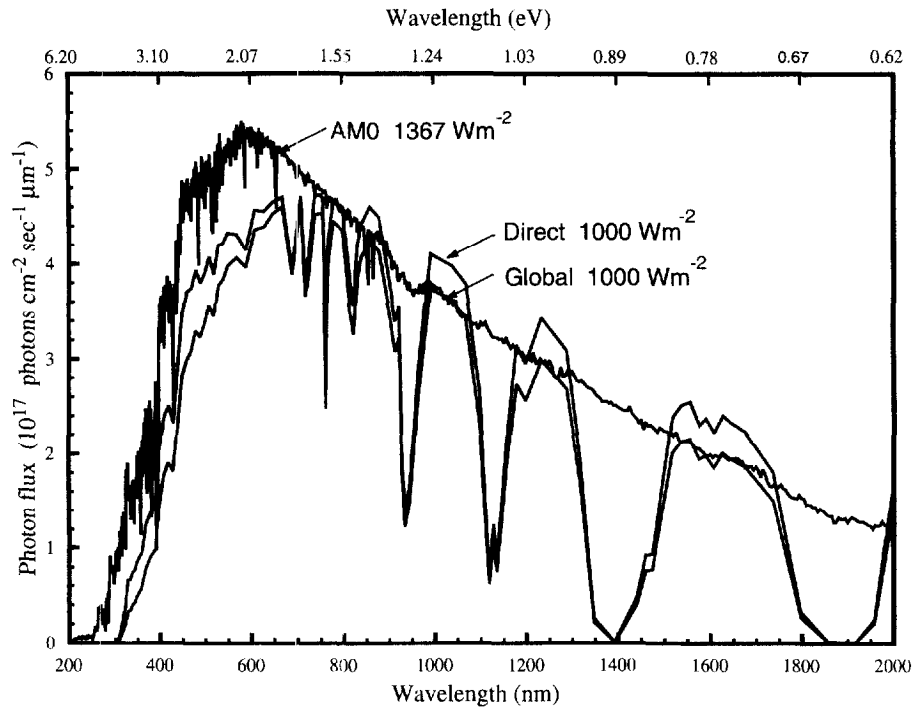


Fig. 2. Comparison of AM0 and standard AM1.5 global spectra, direct component for the terrestrial spectrum.

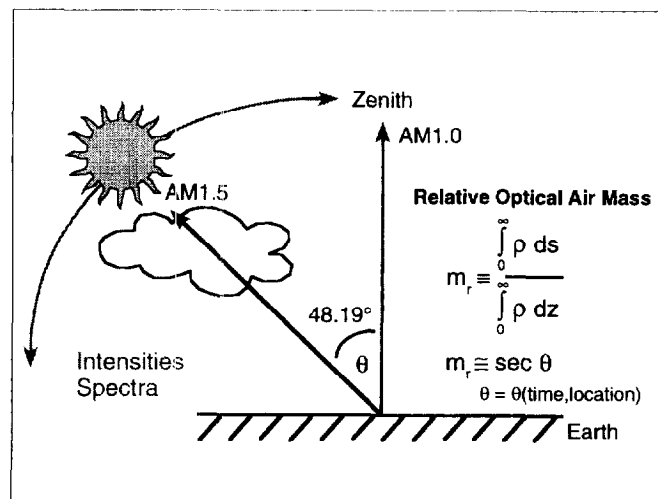


Fig. 3. Illustration and the definition of air mass.

the device and the sun (outer space), and AM1.5 has the sun at an angle of  $48.19^\circ$  to the device normal. The global spectrum has two components: direct and diffuse [62, 63]. Once the photons enter the atmosphere, they are prone to scattering and absorption, leaving gaps or bands in the spectrum due to  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{O}_3$ , and other species [62, 63]. Some simulators are well matched to the standard spectrum through the use of filters to define power densities over a selected area. However, there is no perfect simulator match, and spikes and other irregularities must be considered [62]. To obtain an accurate measure of the cell or module performance, the spectrum of the light source must be known—and this can be measured by a number of instruments (which introduce some measurement uncertainty). One method to ensure that the cell is measured with respect to the standard spectrum is to correct the measurement analytically. The spectral *mismatch factor* is the error in the measured current of the solar cell due to differences between the light source spectral irradiance and the reference spectral irradiance, and the differences in spectral response between the unknown or test cell and the reference cell [64–66]. If the spectral distribution and irradiance of the light source, the spectral response of the device, and the standard spectrum are known, the efficiency can be accurately evaluated by complex, but straightforward, corrective methods [31, 38, 64, 66, 67].

*Procedures.* The methods for determining the efficiencies of cells and modules has been discussed in the publications of standards and in handbooks relating to this issue [31, 65, 66, 69]. The determination of the current-voltage ( $I$ - $V$ ) characterization under these conditions is not trivial, and the expertise and experience of the measurement engineer/scientist is as important as the knowledge and use of the standards. The literature is rich in inaccurate efficiency reports that are “under standard conditions”, but are incorrect because of experimental procedure. For example, one can inadvertently “influence” the fill-factor of the  $I$ - $V$  characteristic by adjusting the sweep rate and direction.

The procedures for obtaining the  $I$ - $V$  characteristics of cells and modules have been documented extensively. The instrumentation is significant, and the cost and precision varies with variable load, current measurement, or voltage measurement method [31]. The methods for obtaining the spectral response or quantum efficiencies also vary, with the filter wheel (higher intensity and illumination area) and monochromator (extended wavelength ranges) techniques being the most common industry standards [70, 71]. To minimize temperature-control problems, pulsed-light simulators are used [73]. However, these can introduce other problems associated with capacitive effects. Laboratories are starting to use large-area, continuous-light simulators and are imposing the spectral-correction methods for cell-performance evaluation on these large-area devices. The complicating factor is the cost for controlling the module temperature.

### 2.3. Concentrators and multiple-junction devices

Cells in concentrated light or cells having more than one junction provide complications for performance evaluation [31]. The efficiency of a photovoltaic concentrator is determined using the area of that cell designed to be illuminated when the cell is mounted in the concentrator module [34]. The concentrator module area is the total area of the concentrating optics. Artificial enhancement of the efficiency can result if the areas external to the cell area are illuminated, although these effects can be eliminated by placing an aperture close to the cell to define the exact area during measurement [73, 74]. The direct-normal irradiance, used in evaluating the performance of concentrator modules or cells (Table 1), can provide an artificial boost in the observed performance compared to flat-plate equi-

valents. However, it is reasonable to base the efficiency of a concentrator cell on a direct-normal reference spectrum and total irradiance, because this is the illumination that the concentrator cell experiences in operation. However, in sunlight operation, there is an added loss in power output because the diffuse component is not used. A number of  $I$ - $V$  measurement problems originate from the high irradiance level and high current densities [75]. The concentrator cell is particularly susceptible to artifacts related to series resistance resulting from the high current densities. The irradiance incident on the cell is the largest source of measurement uncertainty. This arises from the non-uniformity illumination spatial profile and chromatic aberrations associated with the concentrator optics [76–80]. The unavailability of dependable linear-irradiance detectors with identical spatial characteristics and spectral response of the cell also provides a source of measurement uncertainty [80, 81]. Contacts (effects on cell series resistance at higher intensities) and temperature non-uniformities (high injection effects, spatial voltage distributions) are additional concerns for accurate measurements.

Multiple-junction (termed “tandem” or “multijunction”) devices are developed in thin-film and crystalline solar-cell technologies to obtain enhanced performance (efficiency, stability) [81–86]. The efficiency measurement of such structures with respect to standard reporting conditions is generally more complicated than for single-junction devices [31]. Cells having three or more junctions can be evaluated in a straightforward manner, provided that the junctions can be measured separately [87]. For monolithic, multiterminal cells, the measured  $I$ - $V$  characteristics can be functions of the junctions not being measured. Two-terminal multijunctions may have spectral mismatches that lead to bias dependencies [87, 88]. Methods have been developed to obtain the  $I$ - $V$  characteristics (and efficiencies) of multijunctions with respect to the standard reporting conditions, and two such simulators [89, 90] use (1) separate light sources and reference cells for each junction and (2) selected filters on a single simulator. Fiber-optic delivery of selected spectral light sources is also used. The current technologies have uncertainties that exceed those for single-junction performance evaluations (Table 2). However, this remains an area of concern and activity for the measurement scientist because the area of multijunction solar cells remains a viable and growing entity in the technology.

The performances reported in this paper conform to those determined at the various standard test and measurement laboratories worldwide. These organizations collaborate periodically and intercompare their measurement procedures and results to ensure uniformity. Other parameters that have been reported under non-standard conditions are noted. The reason for applying this criterion in this review is to provide for an equitable comparison of the various technologies and to assess their advancement.

### 3. SINGLE-CRYSTAL AND POLYCRYSTALLINE SILICON

Silicon has been and continues to be the foundation of the PV industry. The material is abundant, comprising about 20% of the earth’s crust. Because of its importance to the electronic markets, more is known about the electrical, optical, chemical, and physical properties of this semiconductor than any other material. Silicon solar cells have demonstrated reliability for both the space and terrestrial environments [91–100]. Examination of its fundamental characteristics (i.e. lower than ideal bandgap for terrestrial use, indirect-bandgap type with lower absorption coefficients) might have redirected interest in Si for PV from a theoretical viewpoint. However, these cells have provided among the highest

single-junction efficiencies and short-circuit densities among PV material options. The major limitation to Si has been cost, rather than performance. Much of the industry and research activity in this technology has been guided towards (1) lowering the materials and cell processing costs (including specific attention to alternative Si source materials and improving the manufacturing yields, handling, and steps) and (2) improving the operational performance of the device to near-theoretically predicted values. The research in the latter area has been so successful that the theoretical limits have had to be carefully re-evaluated to provide a more accurate target for the device designers based upon better known materials properties and device/interface characteristics [100].

### 3.1. Single-crystal silicon cells

Until the mid-1980s, an identifiable and wide breach existed between the predicted performance of single-crystal Si cells and the attainable values. This gap was larger than for other technologies, such as GaAs, and many device experts were skeptical that 17–18% terrestrial cells could be produced. In this period, better quality Si (high-purity float-zone) and intense activities in cell modeling and design led to the evolution of efficiencies to beyond 20%. Today, large-area, laboratory cells exceeding 23% have been confirmed, and module efficiencies more than 20% have been demonstrated [101–111]. Table 3 provides a summary of confirmed Si solar-cell efficiencies and related parameters.

The evolution of the high-efficiency Si solar cell is illustrated in the device cross-sections shown in Fig. 4. The relatively simple, conventional  $p$ – $n$  junction of Fig. 4(a) has become more complicated in design and structure. The evolution of a device structure represents the intense attention to device engineering. The purpose is (1) to improve the collection of the incident light by minimizing the front contact area, by improving the antireflection characteristics, and by (in some cases) providing multiple passes for the light with back reflectors to ensure the creation of electron–hole pairs; and (2) to improve the collection of the carriers by incorporating back-surface electric fields to reflect minority carriers that were not previously collected.

The earlier metal/insulator/ $n$ -type/ $p$ -type (MINP) and passivated-emitter solar-cell (PESC) designs by Green *et al.* [100–102], Figure 4(b), (c) demonstrated efficiencies up to 21%. These cells have especially high  $V_{oc}$  and have been fabricated in relatively large areas. Swanson *et al.* [103–109], making use of the previous work on “dot-contact” designs, have had cells verified in excess of 22% using the structure in Fig. 4(d). These cells have all contacting through the back side, so that no light is obscured by a front contact. Problems with high currents associated with this all-back contact design resulted in some minor degradation effects. Figure 5 shows the characteristics of a 22.5% cell, developed primarily for concentrator applications. Cells of this design have been reported with nearly 28% conversion efficiencies under  $100\times$  concentration. A further evolution of the Green PESC cells is the laser-grooved, buried-contact Si cell shown in Fig. 6, and represents a wide range of exceptional device engineering. This cell has front and back surface texturing, a back surface field, and minimal contact area to maximize performance [100, 110, 111]. The double-sided buried-contact (DSBC) is a modification of the first generation single-sided buried-contact (SSBC) design. The newer structure replaces the aluminum rear of the SSBC with boron-diffused grooves and a floating  $n$ -type rear surface. The intent is to improve the rear-surface passivation without the added photolithography step (cost reduction). Cells with  $V_{oc} = 0.671$  V and FF > 0.76 have been demonstrated for this cell in development. The economics of cell process and materials, the engineering problems in concentrator

Table 3. Summary of confirmed Si solar-cell efficiencies and related parameters. Data for a variety of cells are presented to give indications of improvements and scope of device development. Measurements were performed under 25°C, 1000 W/m<sup>2</sup>, ASTM E892 global conditions unless otherwise noted. The area definition used for non-concentrator cells is total area; for concentrator cells, it is the area designed to be illuminated. The independently confirmed efficiencies in this table are from standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Organization	Comments
<i>Monocrystalline silicon</i>							
9/94	4.00	709	40.9	82.7	24.0	UNSW	PERL
4/93	45.70	694	39.4	78.1	21.6	UNSW	PERL
5/96	22.10	702	41.6	80.3	23.4	UNSW	PERL
9/85	1.01	665	36.8	83.6	20.5	UNSW	PESC
10/85	4.02	634	36.3	81.6	18.8	Spire	conventional <i>p-n</i> cell
5/85	1.02	600	31.6	80.7	15.4	Westinghouse	Dendritic Web Si (28°C)
<i>Multicrystalline silicon</i>							
12/95	1.00	636	36.5	80.4	18.6	Georgia Tech	HEM Si
3/93	100.00	610	36.4	77.7	17.2	Sharp	Textured mechanically
<i>Thin silicon</i>							
2/97	1.02				16.6	AstroPower	Silicon-Film™
3/95	240.0	582	27.4	76.5	12.2	AstroPower	Silicon-Film™
11/86	0.120	536	26.0	68.5	9.6	AstroPower	Thin-film Si on stainless steel
8/95	4.04	699	37.9	81.1	21.1	UNSW	47 μm on Si
3/93	100.0	608	30.0	78.1	14.2	Mitsubishi	60 μm on SiO <sub>2</sub>
9/94	4.02	651	32.6	90.3	17.0	ANU	20 μm, thinned Si
5/95	4.00	661	32.8	81.4	17.6	UNSW	CVC Si on Cz Si
<i>Concentrator cells</i>							
5/87	0.15				26.5	Stanford Univ.	Point contact; 140 suns
7/93	1.21				25.7	SunPower	Rear contact; 74 suns
9/90	20.00				21.6	UNSW	Laser-grooved; 11 suns
10/95	1.60				26.8	SunPower	Rear contact. 96 suns

systems, as well as investigation of the operational reliability of this more complex device type are of considerable concern and active investigation. However, the exceptional performance demonstrations have provided the basis for more development of high-efficiency cells of these and other innovative designs and structures.

A related evolution of the engineering of the Si solar cell is the bifacial cells (Fig. 4(e)), which are able to convert sunlight onto both sides of the device surface. These cells, developed by A. Luque, have been investigated for some 25 years [112]. They have the advantages of utilizing reflected light from the surroundings and from static concentrators, but the cell is still not widely adopted—primarily because of complex processing required for the back-side device. Luque and co-workers have developed designs with front and back efficiencies of 18.1% and 19.1% respectively, using float-zone material [113]. Cells on

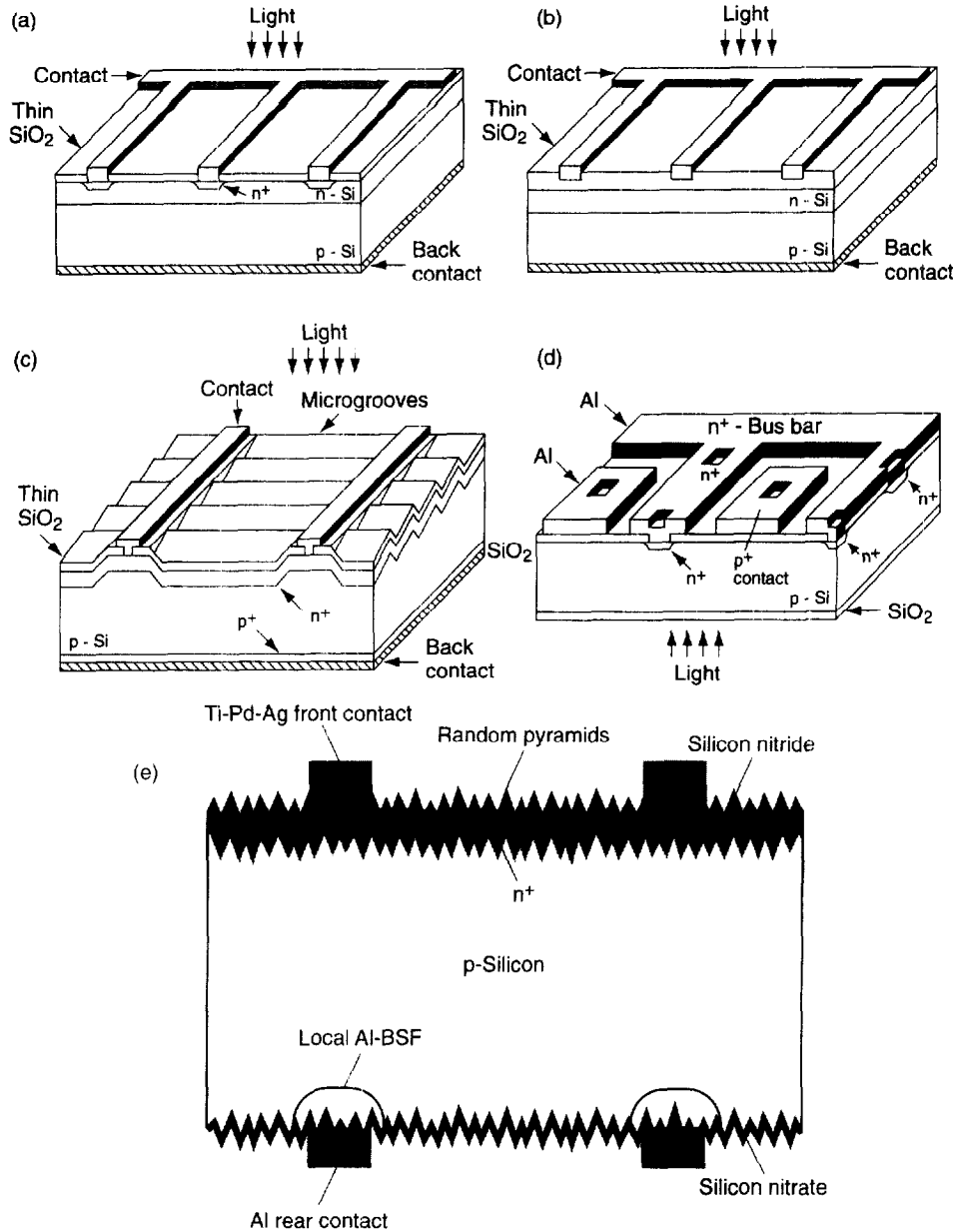


Fig. 4. Evolution of silicon solar cell designs, showing device cross-sections: (a) p-n junction; (b) metal-insulator, n-type, p-type cell (MINP); (c) passivated-emitter solar cell (PESC); (d) point-contact cell; and (e) bifacial solar cell.

Czochralski Si have been realized with corresponding 16.4% and 13.8% efficiencies [114]. The cell in Fig. 4(e) shows a recent design, which implements some of the device engineering used by Green *et al.* for single-sided cells. This configuration is reported to be more cost effective for commercial use, and has best reported efficiencies of 18.4%/18.1% for rear-optimized structures and 19.4%/16.5% for front-optimized versions [115]. The main con-

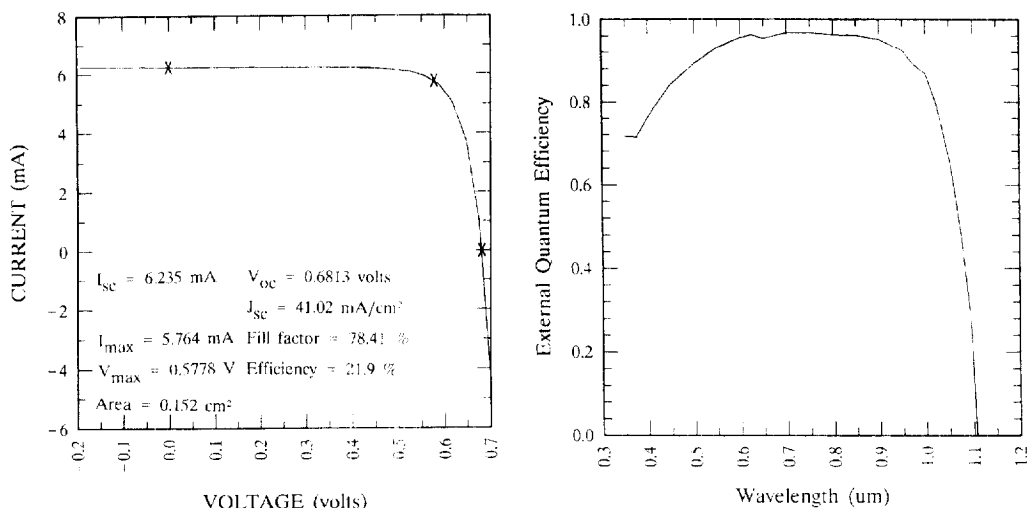


Fig. 5. Performance characteristics of point-contact cell, showing (a) light I-V characteristics, and (b) spectral response.

tribution has been the surface passivation using plasma-enhanced CVD silicon-nitride film. The manufacturing viability and cost effectiveness of this cell design is currently being investigated and considered for further development. The best cells can produce power outputs in the 310 W/m<sup>2</sup> range (using a static concentrator), and if this could be done reproducibly and economically in a module configuration, the bifacial cell might finally receive more serious attention as a commercial product. There is also some argument that even if the rear illumination were low from a reflector (paint, sand), bifacial cells could still provide a useful power gain at little extra cost.

### 3.2. Polycrystalline, multicrystalline, and thin-silicon cells

A major cost factor for the Si cells of the previous section is the production of the high-purity, high-crystalline perfection wafer. This has directed attention toward less energy-intensive processes, which sacrifice the crystalline order and higher device efficiency for the benefits for lower energy production and perhaps the utilization of lower purity feedstock Si leading to decreased product cost. Defects (e.g. grain boundaries, twins, dislocations, voids, etc.) and impurities (especially segregated species) are potential sources for shunts and shorts that limit the current-voltage characteristics of these solar cells [116-120].

NOTE: Some conventions for various crystalline states have been proposed. These are followed in this review: (1) multicrystalline: grain size 1 mm-10 cm; (2) polycrystalline: grain size 1 μm-1 mm; (3) microcrystalline: grain size < 1 μm; and (4) nanocrystalline: grain size < 100 nm. These are consistent with the terminology published by Basore [121], with the addition of the nanocrystalline definition. The Si single crystal is defined with grain size > 10 cm.

Bulk and ribbon approaches for sheet-Si material have undergone extensive investigations and development over the past 20 years [122, 123]. Among these approaches have been casting [124-140], directional solidification [135], the heat exchanger method (HEM) [141, 142], edge-fed film growth (EFG) [143-147], edge-supported pulling (ESP) [148], ribbon-

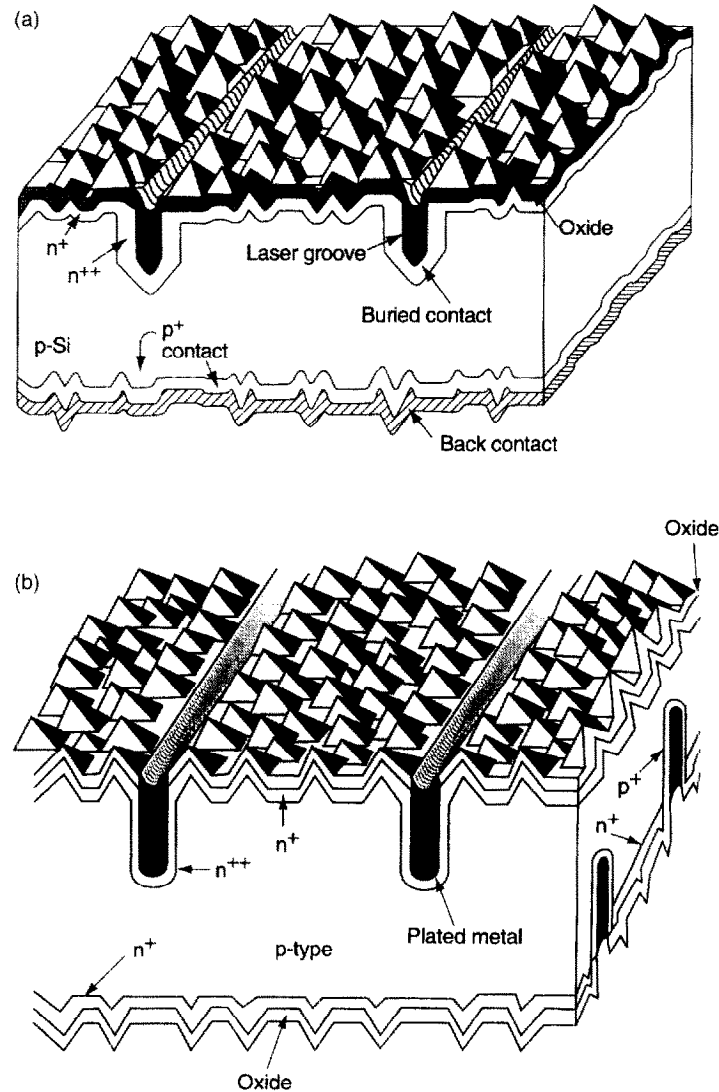


Fig. 6. Laser grooved, buried contact solar cells: (a) single-sided buried contact (SSBC) structure; and, (b) double-sided buried-contact (DSBC) structure.

to-ribbon (RTR) [149], ribbon-against-drop (RAD) [150], spinning [151, 152], dendritic web [153, 154], and low-angle silicon sheet (LASS) [155]. The EFG process has led to a quality commercial product [156–158], and is described schematically and pictorially in Fig. 7. The process involves the shaping of the Si through a special die, forming a connected nonagon or octagon of flat sheets. The cells are cut from the connected structure by laser cutting. Large-area cells with efficiencies exceeding 14% and commercial 12% modules are available for this promising technology. EFG Si technology is in commercial readiness, and is being pursued in several efforts.

Treatments of polycrystalline material and cells with hydrogen, lithium, aluminum,



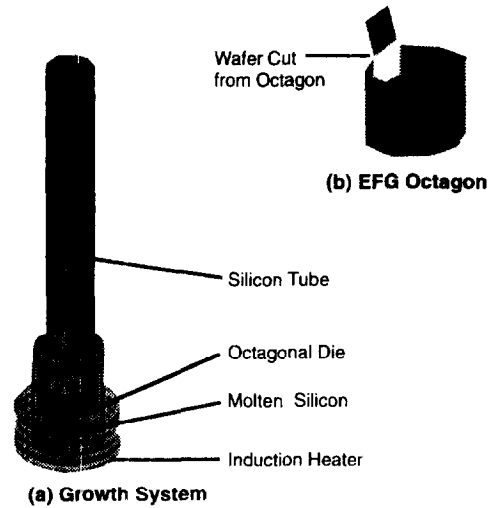


Fig. 7. Edge-fed film growth (EFG) techniques: (a) Schematic representation of the EFG growth of Si sheet; and, (b) illustration of EFG wafer production from octagon.

arsenic, and phosphorus have been used with varying degrees of success in order to minimize the effects of active defects and boundary surfaces [159–169]. The general observation is that these techniques improve the lower efficiency devices, but have far less effect on those having reasonable performances. Much current work centers on understanding chemical interactions among impurities and defects in order to make use of their ability to control material quality. There is considerable effort on identifying those treatment processes that have benefit to commercially produced polycrystalline products, and to implement those treatments into manufacturing processes. The best bulk polycrystalline Si cells have been reported by Rohatgi *et al.* [170], and the performance characteristics are represented in Fig. 8. Green and co-workers have used the MINP structure to produce cells with efficiencies exceeding 17% for this large-grain polycrystalline Si [171].

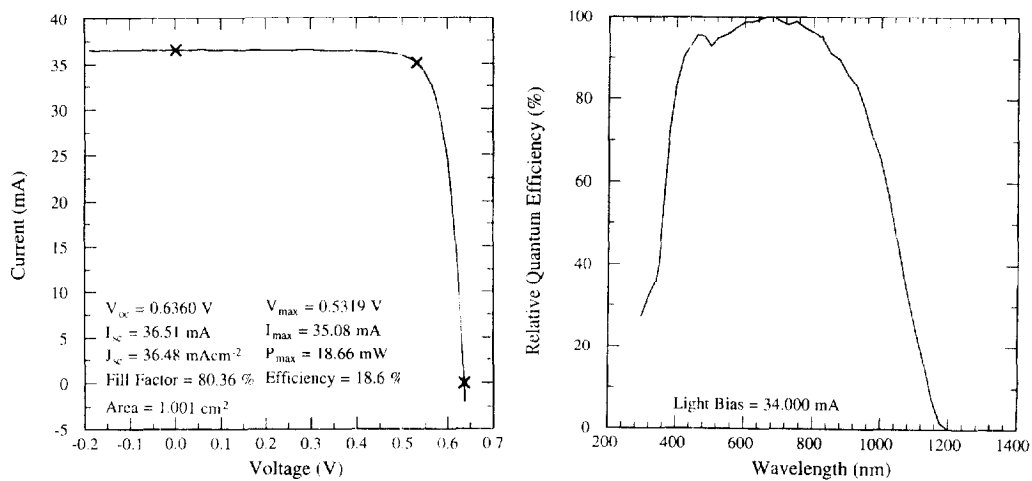


Fig. 8. Multicrystalline Si cell (from HEM Si): (a) light I-V characteristics, and (b) spectral response.

For purposes of better materials utilization, thin-film Si has always been of keen interest to the photovoltaics community. Early attempts at producing thin-film Si cells had been largely unsuccessful, with efficiencies typically in the 5% region [172]. Vacuum deposition required both very high vacuum and rapid deposition in order to minimize oxidation and contamination. Even with the best conditions, cell performances were below expectations [173, 174]. Chemical vapor deposition (CVD), used extensively in the electronics industry, led to some notable successes. Brendel *et al.* reported a 20.6% Si (epitaxy on Si) cell with a thickness of  $47\text{ }\mu\text{m}$  [175]. The exceptional current was attributed (and supported by modeling of the internal quantum efficiency) to a successful light-trapping scheme and back-surface field for this thin Si device. Green *et al.* demonstrated a  $47\text{ }\mu\text{m}$  thinned Si cell (CVD on Si) with an efficiency of 21.5% [176]. The important contribution to this cell was the successful incorporation of enhanced light trapping within the cell. The cell, fabricated in the passivated-emitter, rear locally diffused (PERL) structure, presented in Fig. 9, clearly showed the effectiveness of geometrical light trapping using an inverted-pyramid texturing. The best performances involve a light-trapping scheme that is designed so that the image pyramid is geometrically located in a position for the total internal reflection of the internally reflected light. (This same geometry for a  $400\text{ }\mu\text{m}$  thick cell resulted in efficiencies in the 24% range, and a comparison of the reported  $I$ - $V$  characteristics for these two cells is presented in Fig. 10.) These thin-Si cells illustrate the potential of device engineering on thin-Si cells, but are not realizations of low-cost approaches. Both use high-quality Si substrates for homoepitaxy of the quality thin-Si layers. They are reported as research results rather than commercial products. An evolution of this approach toward a commercial product is the high-efficiency multilayer thin Si cell reported recently by Zheng *et al.* [177]. This cell was grown on an electrically inert  $p^-$  Czochralski-grown Si substrate. The  $npnpn$  structure, shown in Fig. 11, had a total thickness of only  $17\text{ }\mu\text{m}$ ; the required buffer layer was  $15\text{ }\mu\text{m}$ . The best cell had a  $V_{oc}$  of 664.2 mV,  $J_{sc}$  of  $32.9\text{ mA/cm}^2$ , FF of 0.825, and efficiency of 17.6%.

The economy of Si-film cells requires high-performance *and* low-cost materials, processing, and production methods. Work on using modified liquid-phase growth of Si on special

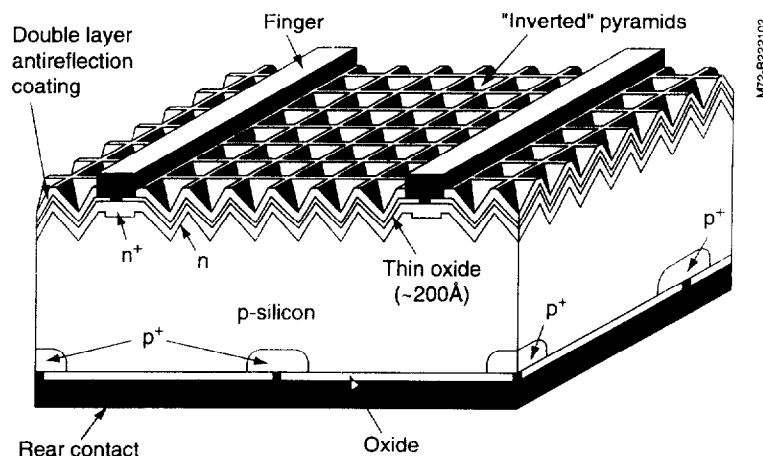


Fig. 9. Recent cell design of passivated-emitter, rear locally-diffused (PERL) structure with a double-layer antireflection coating and inverted pyramids.

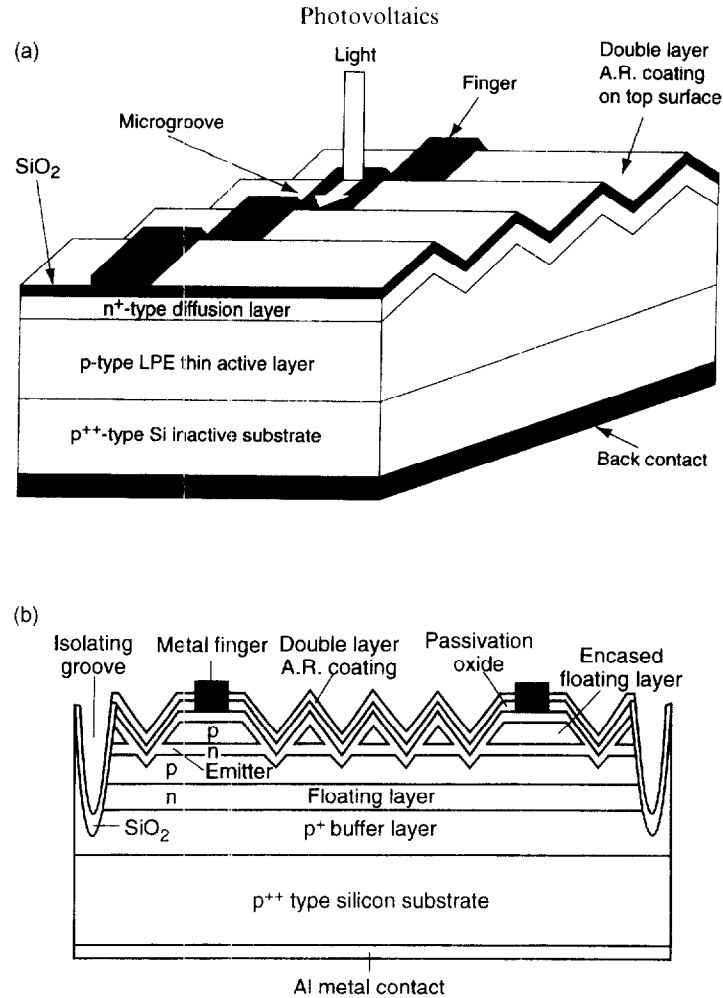


Fig. 10. Structures of advanced thin-film Si cells: (a) thin-film, microgrooved passivated-emitter solar cell (MGPESC); (b) thin-film, multi-layer inverted pyramid passivated-emitter solar cell (IPPESC).

conducting substrates has been reported [179–186]. The approach used some innovative designs to minimize the effects of substrate impurities and inherent film defects. Cells in excess of 12% were reported [179]. However, substrate costs and other factors have modified designs, and recent design modification has led to cells with efficiencies nearly 15% (small area) and large-area devices with efficiencies in the 10% range. Three generations of design, shown in Fig. 12, illustrate the development of this Si-film structure, with the introduction of back-surface reflectors and other device engineering modifications in order to better exploit the photon economy. Commercial products are planned, then are expected when the production capacity and yields of these very promising approaches are increased. Recently an AstroPower Si-film cell with an efficiency of 16.6% has been confirmed [187]. This exceptional device had an area of  $0.98 \text{ cm}^2$ ,  $V_{oc}$  of 0.608 V,  $J_{sc}$  of  $33.53 \text{ mA/cm}^2$ , and an FF of 0.815 (Fig. 13). The device was fabricated from normal manufacturing-line material, and demonstrates the viability of providing very high-efficiency devices from this

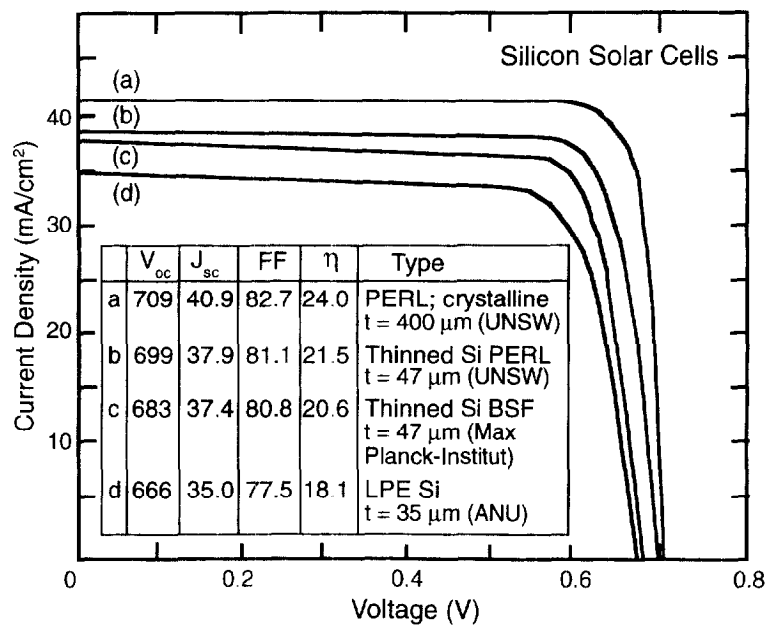


Fig. 11. Comparison of the reported I-V characteristics high-efficiency, thin-layer Si cells: (a); (b); and (c) Light I-V characteristics for thinned epitaxial Si solar cell.

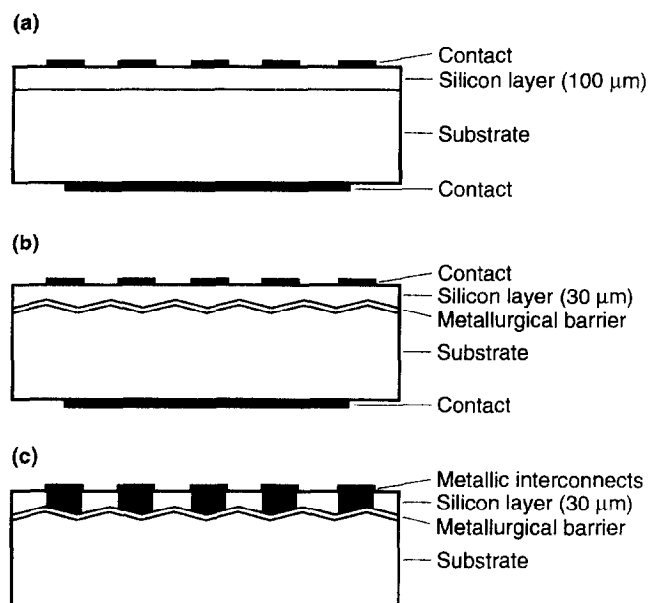


Fig. 12. Silicon-Film<sup>TM</sup> solar cell products, indicating evolution from (a) current design to (b) thinner cell design, and (c) thinner, interconnected cell design.

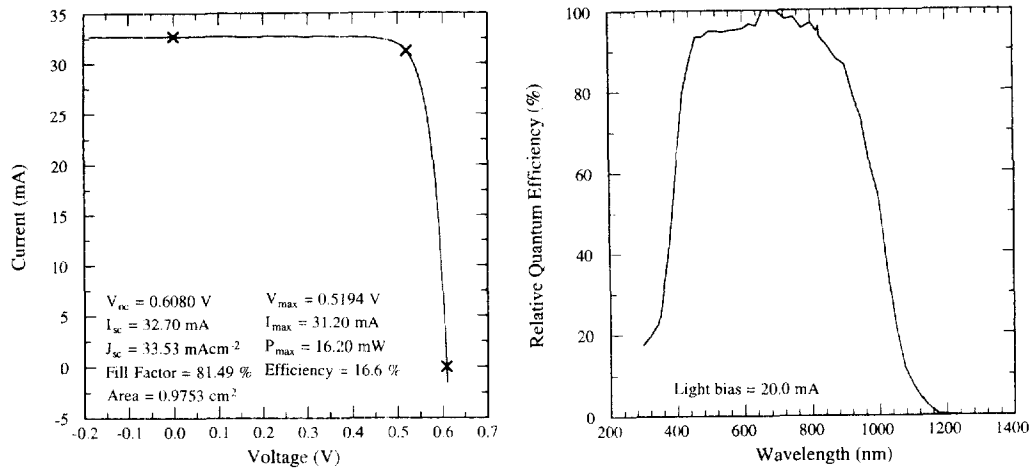


Fig. 13. Silicon-Film™ solar cell light J-V characteristics showing: (a) 16.6% efficiency J-V characteristics for polycrystalline cell; and (b) spectral response.

relatively simple process. The thin Si is produced from inexpensive Si feedstock, and the process itself involves a proprietary controlled-atmosphere heating in a multiple-stage furnace. The Si film is produced continuously, and widths are only limited by the furnace design. Cells of area 1000 cm<sup>2</sup> have been measured with efficiencies of more than 9%, and recently, material of ~30 cm width has been processed into efficient devices—giving film evidence to the practicality and the scalability of this process. A summary of representative thin-film cell performances is included in Table 3.

Silicon-based solar cells continue to lead the industry in performance, availability, and manufacturing. There are issues that threaten the continued advancement in cost-competitiveness. These include materials availability and competition for feedstock resources with the electronics industry. Manufacturing costs remain higher than predictions, and manufacturing capacities are not expanding at the 20-30% per year required to meet the 1 GW per year levels that some analysts predict will be required by 2010. Some photovoltaic experts continue to consider this technology as only an “intermediate alternative”. Silicon cells have also been referred to as “the ultimate photovoltaic solution” [188]. As the technology continues to improve (pushed both by the industry itself and other photovoltaic technology competition) and continues to adjust to changing needs, it will maintain a dominant role in photovoltaics.

#### ISSUES AND CONCERNS: SILICON TECHNOLOGY

- **Silicon feedstock:** Silicon materials issues remain uncertainties for the crystalline Si technology in several areas: (1) Materials availability. The capacity and availability of Si feedstock material is uncertain. Silicon-production forecasts are low and plans for increased production are uncertain for the mid-term, and these factors can adversely affect PV. The major source for PV-feedstock Si is the material “waste” that the electronics industry does not use. With diminishing supplies, these previously discounted sources are either used or recycled for electronic applications. The scarcity

had made such approaches cost effective and profitable for the semiconductor industry, and has reduced lower cost feedstock for photovoltaics. (2) Solar-grade Si. This is an old issue that remains a factor in the development of low-cost approaches. (3) Competitiveness. The semiconductor electronics industry can afford to pay prices much above the \$10–15/kg demanded for a cost-effective PV product. There are many uncertainties about the sources for silicon for all uses, and those for PV uses are especially sensitive. Threats to silicon availability is a periodic scare to the photovoltaic manufacturers—and this issue will continue into the next five years.

- **Manufacturing costs:** Most cost predictions indicate that crystalline Si cannot meet the lower cost requirements of most national programs. Even the mid-term objectives require some investment in improvements with manufacturing methods to increase yields, improve cell device performance, and increase production volume. This may require continued government investment in the near term (e.g. such as recent U.S. programs) to ensure long-term viability.
- **Manufacturing capacity:** The world capacity shipped some 90 MW this past year, about 80% of this being crystalline Si. This capacity is certainly insufficient to meet the projected gigawatts per year demands forecast for even the near term. There are no (~100 MW per year) commitments to increase either manufacturing capacities or Si production capacities to meet these projections in the next 2–5 years.
- **Research:** This technology is proof that device research has a direct impact on making a viable product. Device engineering has led to exceptional device developments and impacted the industry performance standards. Research on materials production, device development, and process improvement will herald the next generation of practical Si devices. Creativity brought Si technology to the fore, similar creativity will herald its advancement.

#### 4. III–V SEMICONDUCTORS

Semiconductors such as GaAs, GaAlAs, GaInAsP, InAs, InSb, and InP have long received attention for photovoltaic applications because they have exceptional, near-optimal, and alterable characteristics [190–192]. Passionate support for III–V photovoltaics is tempered by equally strong expressions of doubt about their terrestrial validity. Knowledge about the properties of these materials has been enhanced because of their use in high-speed and optical electronics. Cost is the usual factor cited for limiting widespread use of III–V solar cells in terrestrial PV. Space markets have expanded as they are less sensitive to cost, but more sensitive to performance and radiation resistance [193]. In this section, III–V cells are discussed in terms of their performance for flat-plate and concentrator modes of operation, since there are good arguments that these approaches will eventually be cost effective.

##### 4.1. *Single-junction approaches*

The first-order economic argument for utilization of these high-value semiconductors in concentrators is that the expensive cell area is decreased in proportion to the irradiance, and the concentration of the light is accomplished by less costly optical components [194]. Most solar cells operate with higher efficiencies under increased irradiance conditions. However, there are some disadvantages. Optical losses (reflection or absorption) in the

focusing lenses and concentrator can account for as much as 10% of the available radiation. Concentrators do not effectively use the diffuse component of the incident sunlight, which constitutes some 18–22% of the available solar energy [194]. Therefore, concentrator systems are more competitive with their flat-plate counterparts in very sunny locations.

Two common structures for high-efficiency GaAs-based cells are shown in Fig. 14. Both are configured to minimize the high surface recombination that is common in direct-bandgap semiconductors [195]. The best efficiencies for these single-junction cells are summarized in Table 4. The performance characteristics (light  $I$ - $V$  and spectral response) of the best confirmed GaAs cells (large and small areas) presented in Fig. 15. It should be noted that a number of organizations have produced GaAs-based cells with AM1.5 efficiencies in excess of 21% and having large areas. These efficiencies are typically higher under concentration (Table 4).

High-quality III–V semiconductors are typically grown by metal–organic chemical vapor deposition (MOCVD) [196]. This growth method has been the foundation of high-efficiency cell R&D, and has been the one used for the highest performance devices. It is versatile, extremely controllable, and able to meet both large-area and high-production capacity goals. Molecular-beam epitaxy (MBE) has contributed primarily to research efforts, but has not been common to commercial activities (i.e. space cells) [197]. Several other deposition techniques have been utilized, but none has been as successful as MOCVD in growing reproducible, high-quality material over large areas. One promising development was the cleavage of the lateral epitaxial film technology (CLEFT) process [198–200], which allows the reuse of expensive substrates. Developed by Fan *et al.* in the mid-1980s, the process involved the growth of a MOCVD GaAs film on a GaAs substrate, onto which a thin,

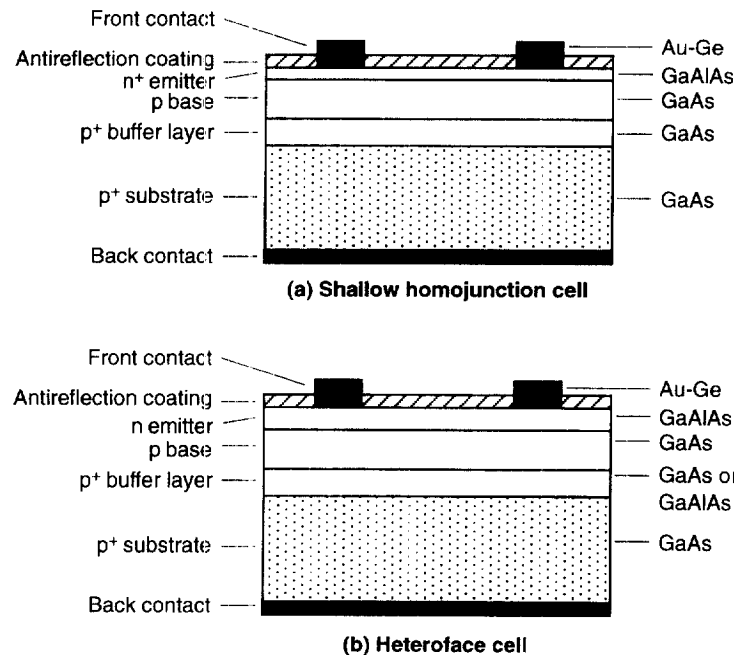


Fig. 14. Two common structures for high-efficiency GaAs-based cells: (a) shallow homojunction; and (b) heteroface cell.

Table 4. Summary of confirmed III-V solar-cell efficiencies and related parameters. Data for a variety of cells are presented to give indications of improvements and scope of device development. Measurements were performed under 25°C, 1000 W/m<sup>2</sup>, ASTM E892 global conditions unless otherwise noted. The area definition used for non-concentrator cells is total area; for concentrator cells, it is the area designed to be illuminated. The independently confirmed efficiencies in this table are from standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Organization	Comments
<i>One sun cells</i>							
3/89	4.003	1035	27.57	85.3	24.3	ASEC	GaAs, GaAlAs window
11/89	4.00	1011	27.55	83.8	23.3	Kopin	GaAs Cleft (separated)
3/90	3.91	1022	28.17	87.1	25.1	Kopin	GaAs, GaAlAs window
4/90	16.00	4034	6.55	79.6	21.0	Kopin	GaAs Cleft 5 mm (submodule)
7/85	1.01	8.22	19.7	62.2	10.1	SMU	Thin-film
3/89	0.25	1018	27.56	84.7	23.8	Spire/Purdue Univ.	GaAs/Ge/graphite MBE GaAs
3/89	0.25	1029	27.89	86.4	24.8	Spire	GaAs, GaAlAs window
4/90	4.02	878	29.29	85.4	21.9	Spire	InP
11/88	0.25	1190	23.8	84.9	24.1	Spire	GaAs/Ge tandem
4/92	16.14	1035	26.9	85.4	24.2	Spire	GaAs (large-area)
3/89	0.500	2403	13.96	83.4	17.6	Varian	Two-terminal tandem
	0.500	1402	13.92	86.8	16		1.93 AlGaAs top cell
	0.531	1000	13.78	83	11.3		GaAs bottom cell
					27.3	Varian	Three-terminal tandem (total)
3/89	4.000	1045	27.6	84.5	24.4	Varian	GaAs, GaAlAs window
8/90	0.310	876	28.7	82.9	20.9		InP top cell
	0.312	337	21.94	72.1	5.3		0.75-eV GaInAs bottom cell
					26.2	NREL	InP/GaInAs 3-terminal tandem
6/93	0.250	2385	13.99	88.5	29.5	NREL	GaInP/GaAs 2-terminal tandem
12/89	0.250	1049	28.5	84.4	25.3	NREL	GaAs heteroface, GaInP window
8/88	0.108	813	27.97	82.9	18.9	NREL	ITO/InP
4/96	4.00	2488	14.22	85.6	30.3	Japan Energy	GaInP/GaAs 2-terminal tandem
<i>Concentrator</i>							
9/88	0.317	--	--	--	29.6	Varian/Standford/Sandia	GaAs/Si, 350 suns Four-terminal mechanical stack
10/89	0.053	--	--	--	32.6	Boeing	GaAs/GaSb, 100 suns Four-terminal mechanical attack



Table 4. Continued

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$ (%)	Efficiency (%)	Organization	Comments
3/93	41.4	—	—	—	25.1	Boeing	GaAs/GaSb 3 mechanical stacked cells, 57 suns
5/91	0.250	1154	4988	86.4	27.6	Spire	GaAs, 180 suns
	0.126	—	—	—	27.6	Spire	GaAs, 255 suns
5/91	0.250	1065	5911	80.2	21.3	Spire	GaAs/Si, 237 suns
1/91	0.0746	959	1509	87.3	24.3	NREL	InP homojunction, 52 suns
2/91	0.0746	899	6343	82.5	27.5	NREL	1.15-eV GaInAsP, 171 suns
12/94	0.103	2663	2320	86.9	30.2	NREL	GaInP/GaAs 2- terminal, 178 suns
10/90	0.0511	1096	990.3	83.5	23.1		GaAs top cell, 39.5 suns
	0.0534	626	556.7	80.7	7.1		0.9-eV GaInAsP under GaAs
					30.2	NREL	Four-terminal InP/GaInAs tandem
8/90	0.0634	973	1416	83.8	22.9		InP top cell, 50 suns
	0.0662	445	1312	75.7	8.9		0.75-eV GaInAs bottom cell
					31.8	NREL	Three-terminal InP/GaInAs tandem

lithographic carbon-based grid layer is produced. This allows the GaAs to nucleate on the substrate, fill the gaps, and then grow laterally across the surface of the carbon-based film. After 2–10  $\mu\text{m}$  of the GaAs is grown, it can be separated or cleaved from the reusable substrate. Cells in excess of 20% efficiencies are demonstrated using this technique, but the method has never attracted substantial investments from the III–V industry for solar cells.

Much of the work on InP cells has been directed toward space applications, primarily because of the cell's high efficiency and radiation resistance [201–210]. Work on InP for terrestrial utilization was essentially abandoned in the early 1980s because of the extreme high cost of the starting single crystals, the difficulty of growing and controlling the properties of these crystals, and the inability to produce device-quality thin films. Cell efficiencies in excess of 21% have been reported for homojunctions, with several confirmed results in excess of 20% AM1.5 [211]. Alternative approaches using thin conductive oxides to produce either heterostructures or shallow homojunctions have also shown promise, with the best cells having AM1.5 efficiencies of 18.5% [212, 213]. It is unlikely that InP will be a major player in the terrestrial market.

#### 4.2. Multiple-junction devices

To realize the extreme performance limits (i.e. concentrators approaching 40% efficiency), alternative approaches to photovoltaics have been pursued [214]. Single-junction cells are constrained by the second law of thermodynamics to efficiencies below  $\sim 30\%$  for common device configurations [215–217]. The concept of a multiple-junction or tandem arrangement

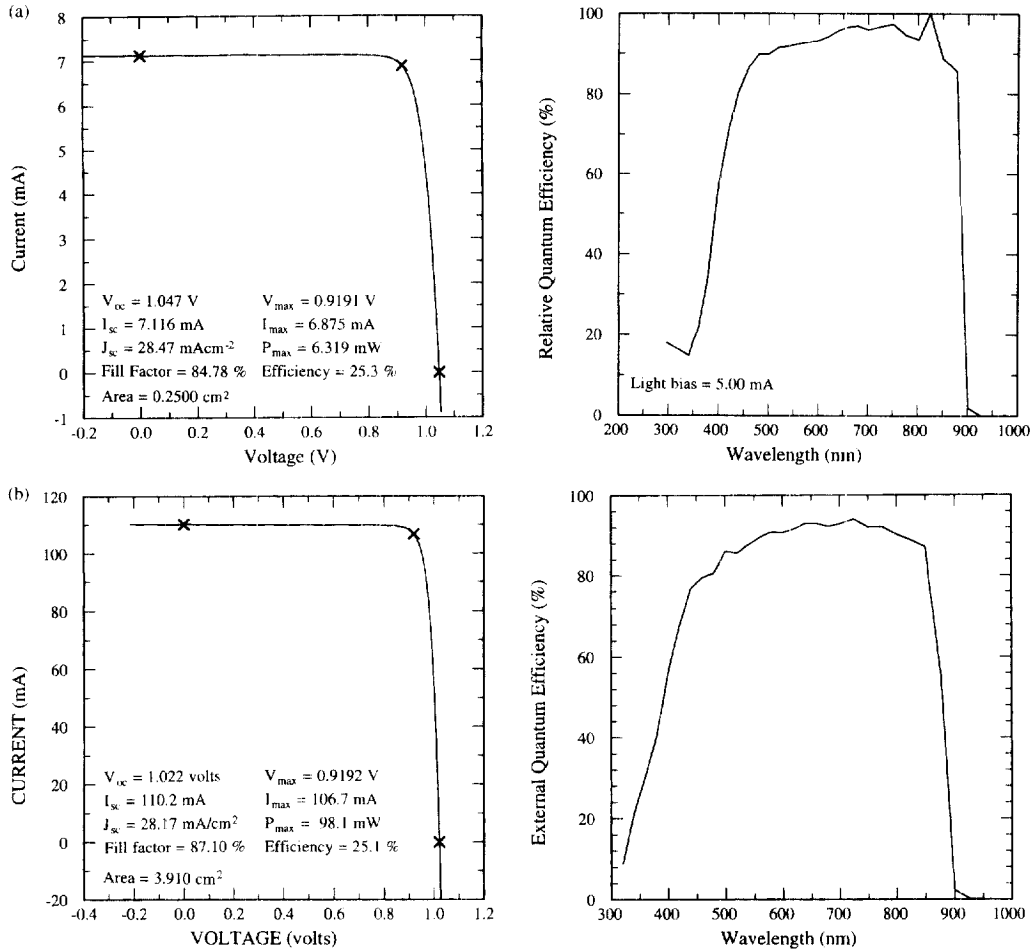


Fig. 15. Performance characteristics (light I-V and spectral response) of the best confirmed GaAs cells: (a) 25.3 %, 0.25 cm<sup>2</sup> device; and (b) 25.1 %, 3.91 cm<sup>2</sup> device.

is simple. If two or more solar cells are stacked in such a way that the portion of the light not absorbed passes through the top cell and is utilized by the bottom device, the solar spectrum can be more effectively used, and increased efficiencies can be obtained. The cascade system can use cells of differing semiconductors which respond to different portions of the solar spectrum. The spectral splitting approach employs special optics to provide two (or more) separate cells with a different energy portion of the solar spectrum. This system has been demonstrated for Si/GaAs cells by Varian [218], with a reported efficiency of about 28% (with optical losses subtracted). Although developed seriously in the early 1980s, this approach has not received further interest primarily because of the relative cost of the hardware and sensitivity of the system to spectral alignment compared to other multiple-cell approaches. Instead, attention has been primarily directed to a second approach, the tandem configuration which stacks cells.

The tandem configuration really has several options, and these are illustrated in the cell

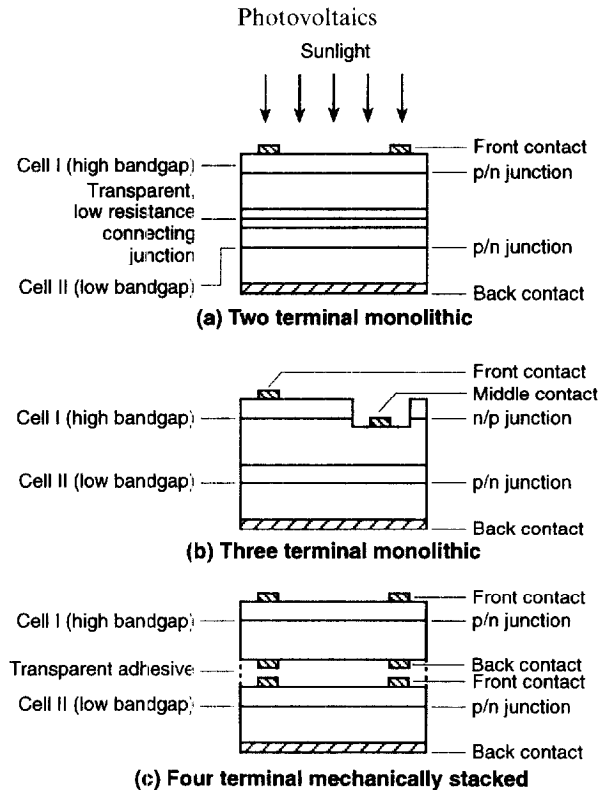


Fig. 16. Multiple-junction structures for high-efficiency solar cells: (a) two-terminal; (b) three-terminal; and (c) four-terminal.

structures of Fig. 16. The first is a completely integrated structure or two-terminal tandem, presented for a two-cell arrangement (Fig. 16(a)). A major problem is the identification and fabrication of the conducting region which has adequate electrical properties as well as sufficient optical transparency for the bottom cell. A usual technique is to use a tunnel junction. This has been significantly developed over the past 10 years and has overcome some initial problems with stability in these configurations [219, 220]. A second approach is the three-terminal cascade cell, shown in Fig. 14(b). Problems with voltage matching initially impeded development of this cell [221], but progress has led to some high-efficiency realizations of this structure. The third approach, the four-terminal connection, has the cells completely separated (Fig. 16(c)). The top cell is sufficiently transparent (both top and bottom contacts) to allow the required long-wavelength light to be incident on the bottom device. This approach has several advantages, including a larger number of semiconductors available for optimal utilization. All three of these approaches have undergone extensive modeling [222–225], from which predictions of optimum bandgaps for the top and bottom cells are made. These have proved to be very accurate, and the analytical calculations have formed the basis for several  $> 30\%$  multijunction solar cell demonstrations.

Single-crystal III–V tandems were first reported in the early 1980s, with an AlGaAs (1.9 eV)/GaAs cell yielding a 16.5% efficiency [226]. The bandgaps of this cell are not ideal. It was developed to demonstrate the concept based upon available III–V growth technology. Several AlGaAs/GaAs cells yielded efficiencies in excess of 20% in the mid-1980s under

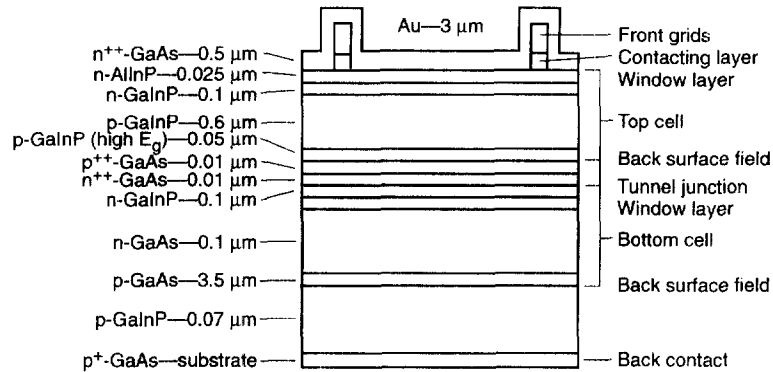


Fig. 17. Cross-sectional representation of high-efficiency GaAs/GaInP solar cell.

concentrated light [227, 228]. At this same time, Fraas *et al.* developed a GaAsP/GaAsSb tandem, with a 22% efficiency [229]. This early work provided (1) a critical understanding of processing the III-V semiconductors, especially in these multilayer configurations and (2) a demonstration of the concept that tandem designs work.

The work on these multiple-junction III-V cells accelerated with the work of Olson *et al.* on GaInP/GaAs tandems. The first cell at 21.8% had not only a credible performance, but also a large (1 cm<sup>2</sup>) area [230]. Within a year, this cell design reached 25.1% [231], and heralded a flurry of activity in pursuit of the 30% efficiency “barrier”. Their champion efficiency III-V monolithic two-junction device is the GaInP/GaAs cell, with an efficiency of 29.5% (AM1.5) and 30.2% (180 suns concentration) [232]. The structure of this cell is presented in Fig. 17, and the *J-V* and spectral-response characteristics are included in Fig. 18. Recently, Takamoto *et al.* produced a 30.2% (AM1.5) cell, using a similar GaInP/GaAs structure for a 4 cm<sup>2</sup> monolithic tandem cell [233]. Other significant multijunction accomplishments include a three-terminal, monolithic InP/GaInAs tandem cell at 31.8% (100 suns) and a four-terminal, mechanically stacked GaAs/GaInAsP cell at 30.2% (40

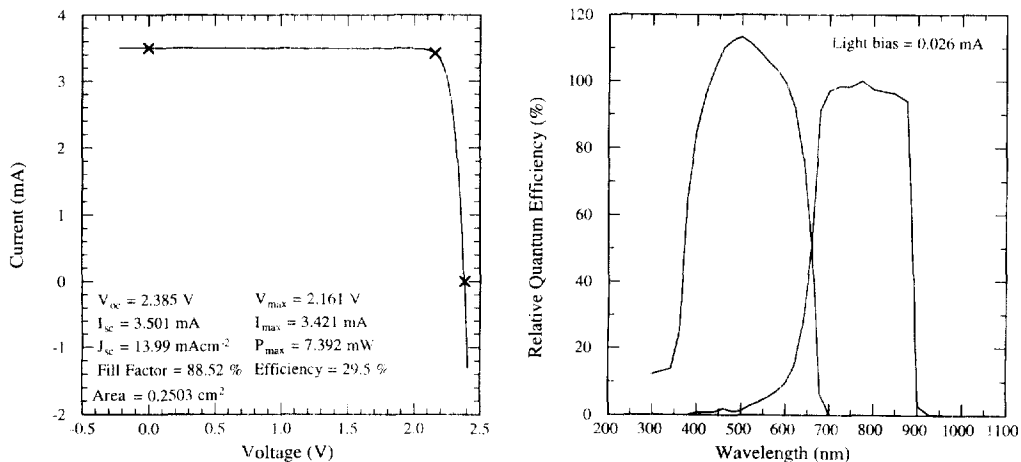


Fig. 18. Two-terminal, 29.5% (AM1.5) GaAs/GaInP solar cell: (a) light *I-V* characteristics, and (b) spectral response. Cell structure shown in Fig. 17.

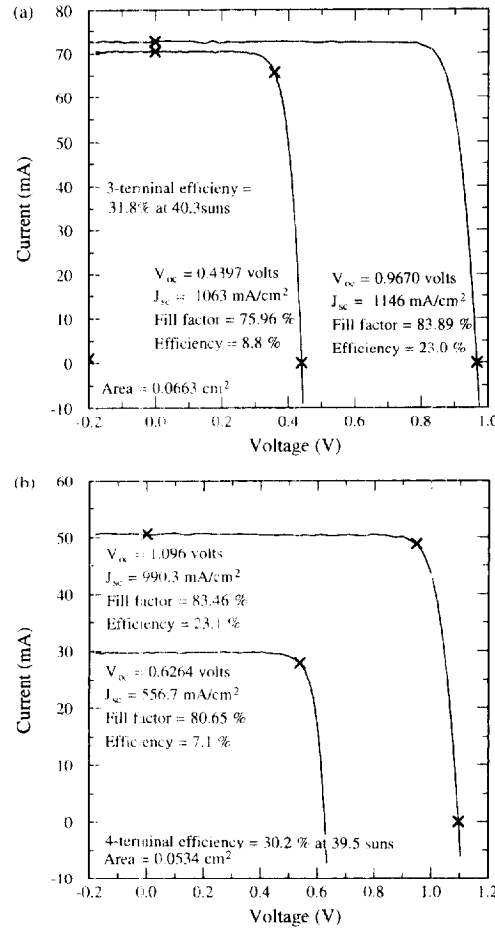


Fig. 19. High-efficiency concentrator cells: (a) Three-terminal J-V characteristics for 31.8 % device (40.3 suns); and (b) Four-terminal (mechanical stack) J-V characteristics for 30.2 % cell (39.5 suns).

suns), both by Coutts and co-workers [234, 235]. Both cell structures are compared in Fig.19. Multiple-junction devices measured near 30% include the Boeing GaSb/GaAs four-terminal tandem with a 34% efficiency under 100 suns concentration [236], and a GaAs cell stacked mechanically on Si—measured at 29.5% at 350 suns [237]. The performances of these and other tandem devices are summarized in Table 4. While these robust performing solar cells boast the highest efficiencies, the cost demands for terrestrial markets are still impeding their acceptance in competition with other approaches. Certainly, they have immediate consideration of high-value applications such as space power.

#### ISSUES AND CONCERNS: III-V TECHNOLOGIES

- **Cost:** The major concern with GaAs and other III-V technologies is the cost for terrestrial applications. This includes materials, manufacturing, and processing costs.

- **Industry:** The major industry installations are directed toward space applications, and do not have a significant capacity that could be directed to provide a significant portion for terrestrial needs. A viable near-term application, concentrators, has a small industrial base, and the vast majority of that uses Si cells. There is almost no demonstration of III–V solar cells in a terrestrial application.
- **Research:** These semiconductors have vast research interest and an extraordinary base in the world. This is partially due to the interest in these semiconductors for other electronic applications. III–V semiconductors may have the strongest research base (though little is concerned with PV), ranging from fundamental through applied research. It is the lack of industry and government interest for photovoltaics that has limited development. Recently, some added interest in polycrystalline III–Vs has spurred some investment. These semiconductors did receive some attention in the late 1970s and 1980s, but are embryonic in their development for any device application like a solar cell. Other related technologies, such as thermophotovoltaics and space PV, may be the incubator and holding space for the III–Vs until some future time.

## 5. POLYCRYSTALLINE THIN FILMS

The arguments for thin-film devices for terrestrial PV are primarily based on materials utilization (less required and more efficient module-area coverage), large-scale manufacturing potential, and better energy economy for production [31, 238, 239]. Additionally, cost and performance advantages can be realized by using “other than Si” semiconductors in such thin layers (see Appendix I). The first serious thin-film cells,  $\text{Cu}_2\text{S}/\text{CdS}$  (sometimes miscalled “the cadmium sulfide cell” even though the active cell layer is the cuprous sulfide), were actually developed for space applications with the promise of better power-to-weight ratios—especially important for early satellite missions [24]. Reliability problems virtually eliminated work on this particular cell type for both space and terrestrial considerations, even though  $1\text{ cm}^2$  cells with efficiencies in excess of 10% were achieved, and several commercial companies were established to produce and market this technology [239–241]. This section focuses primarily on compound semiconductor thin-film approaches (thin silicon having been covered earlier).

### 5.1. *Copper indium diselenide and other Cu ternaries*

Interest in Cu-ternary semiconductors for solar-cell applications began in the early 1970s, precipitated by the questions that existed with both the Si and  $\text{Cu}_2\text{S}/\text{CdS}$  cells [242, 243]. New and less-studied PV materials were undergoing increased scrutiny during this period. Among these, I–III–VI<sub>2</sub> and II–IV–V<sub>2</sub> chalcopyrites received serious attention and the Cu ternaries evolved as attractive candidates after the demonstration of  $n\text{-CdS}/p\text{-CuInSe}_2$  as a broadband optical detector [244, 245]. The performance potential of the Cu-ternary semiconductors is associated with their desirable properties for terrestrial application [246]. Three had initially received most attention,  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ , and  $\text{CuInTe}_2$ , because:

- (1) their bandgaps have satisfactory values for either homojunction or heterojunction (with a wide bandgap window) device types [247];

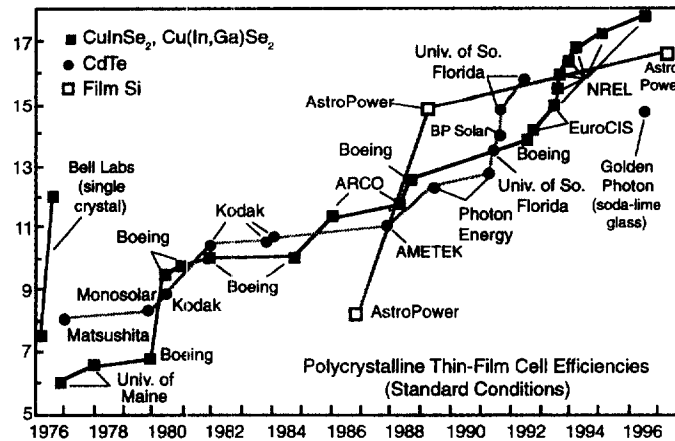


Fig. 20. Evolution of the  $\text{CuInSe}_2$ -alloy and  $\text{CdTe}$  solar cells over the period 1975 to 1996. Also shown are the Silicon-Film<sup>TM</sup> and single-crystal  $\text{CuInSe}_2$  cells.

- (2) their bandgap transitions are direct, minimizing the requirements for minority-carrier diffusion lengths and absorber-layer thickness [248];
- (3) *n*- and *p*-type material can be produced (except possibly for the  $\text{CuInTe}_2$ ) with wide ranging electro-optical properties [249];
- (4) the lattice and electron affinity matches are suitable with common *n*-type windows (e.g.  $\text{CdZnS}$ ,  $\text{ZnO}$ ,  $\text{ITO}$ )—although some valid arguments exist that these properties may not be as important for polycrystalline thin-film cells [250];
- (5) the optical absorption coefficients (Fig. 30) are extraordinarily high, with measured values for  $\text{CuInSe}_2$  ( $1\text{--}5 \times 10^5 \text{ cm}^{-1}$ ), the highest reported among semiconductors [251–254];
- (6) the electro-optical properties are extremely stable, even when exposed for long times to normal (e.g. laboratory) environments [255].

The evolution and development of the Cu ternaries for PV have been rather remarkable [256–258]. The advent of the first single-crystal cells (Fig. 20) was only in 1974–75 [244]. Subsequently, thin-film analogues, with efficiencies exceeding 6%, were realized by 1978 [259]. Thin-film cells of  $\text{CdS}$  on  $\text{CuInSe}_2$  (also referred to as CIS), with efficiencies greater than 10%, were confirmed in 1982 [260]. Another major milestone was the EuroCIS demonstration of a new generation of nearly 15% cells in 1993 [261, 262], leading to the best devices which have now reached almost 18% for laboratory or research cells [263–265]. (It should be noted that early cells were measured against the direct, not global, AM1.5 spectrum and were overrated by about 5% before about 1983 because of the higher red content of that spectrum.) Large-area ( $10\text{--}100 \text{ cm}^2$  [266]) cells have not been confirmed in the 11–15% range under standard conditions, giving promising evidence that large-scale manufacturing is feasible for this apparently complicated semiconductor material [267–270].

The structure of the solar cell is somewhat involved, as indicated in the cross-sectional representations of Fig. 21 [271–273]. The layer complexity shown in Fig. 21(a) was originally mandated because if low-resistivity  $\text{CuInSe}_2$  and  $\text{CdS}$  were used throughout the device (as desired for lower series resistance), Cu-cones, filaments, or precipitates tended to form

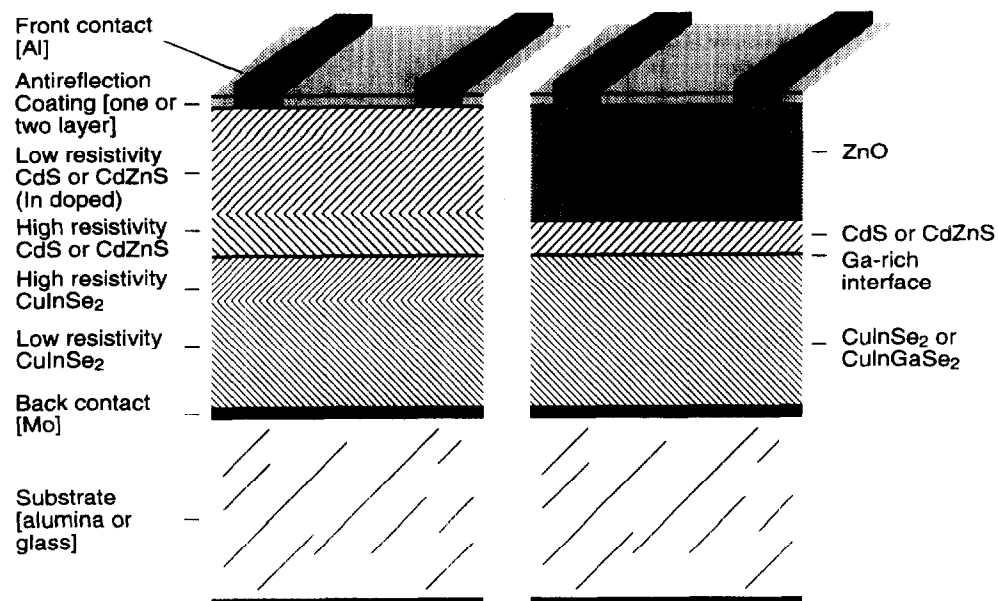


Fig. 21. Cross-sectional representations of  $\text{Cu(In,Ga)Se}_2$  solar cells: (a) with CdS; (b) with ZnO layer.

at the heterointerface (especially for vacuum-deposited layers), destroying the junction properties [260]. In order to increase the bandgap of the 1.02 eV  $\text{CuInSe}_2$ , Ga (substituting for the In) and S (substituting for the Se) are now commonly added to the compound semiconductor formulation, as suggested by Robbins *et al.* [274], Hörig *et al.* [275], and Paorici *et al.* [276] in the 1970s. This led to the investigation of  $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$  films on GaAs by Schuman *et al.* [277] and on ZnSe by Seuret *et al.* [278], the first demonstrations of  $\text{Cu(In,Ga)Se}_2$  heterostructures in photovoltaics with the purpose of improving the open-circuit voltages. Zunger and Jaffe [279, 280] provided extensive and important theoretical studies of the incorporation of Ga into the ternary, including predictions of band structure, bandgaps, and related electro-optical properties. The Ga introduction provides for the unpinning of the Fermi level at the heterointerface. The cross-section shown in Fig. 21(b) is the common design for current cells. Typically, about 25–30% Ga is used, with an associated  $\text{Cu(In,Ga)Se}_2$  bandgap near 1.15–1.20 eV [281]. Higher Ga content (>30%) films do yield higher  $V_{oc}$  cells, but the efficiency is reduced. The reason is not well understood. However, bandgap engineering using high Ga concentrations in the film bulk, but lower at the surface region (producing a concentration gradient) has produced 14–16% cells with  $V_{oc}$  as high as 0.73 V [282]. Light  $I$ - $V$  characteristics for the champion  $\text{CuInSe}_2$ - and  $\text{Cu(In,Ga)Se}_2$ -based thin-film cells, developed by Noufi *et al.*, are presented in Figs. 22 and 23, along with their associated spectral response characteristics [263]. Comparing these cells, the benefit of adding Ga to the absorber can be seen in the value of the open-circuit voltage. However, two features of this cell type require attention for module design: (1) high short-circuit current densities (due to the high absorption characteristics of the semiconductor) [283]; and (2) relatively low open-circuit voltages (attributed to a combination of grain size, film resistivities, chemical effects at the junction and other cell interfaces, and/or back contact origins) [284–286].

The cell itself has been modeled as a heterojunction [287–292], homojunction [293–295],



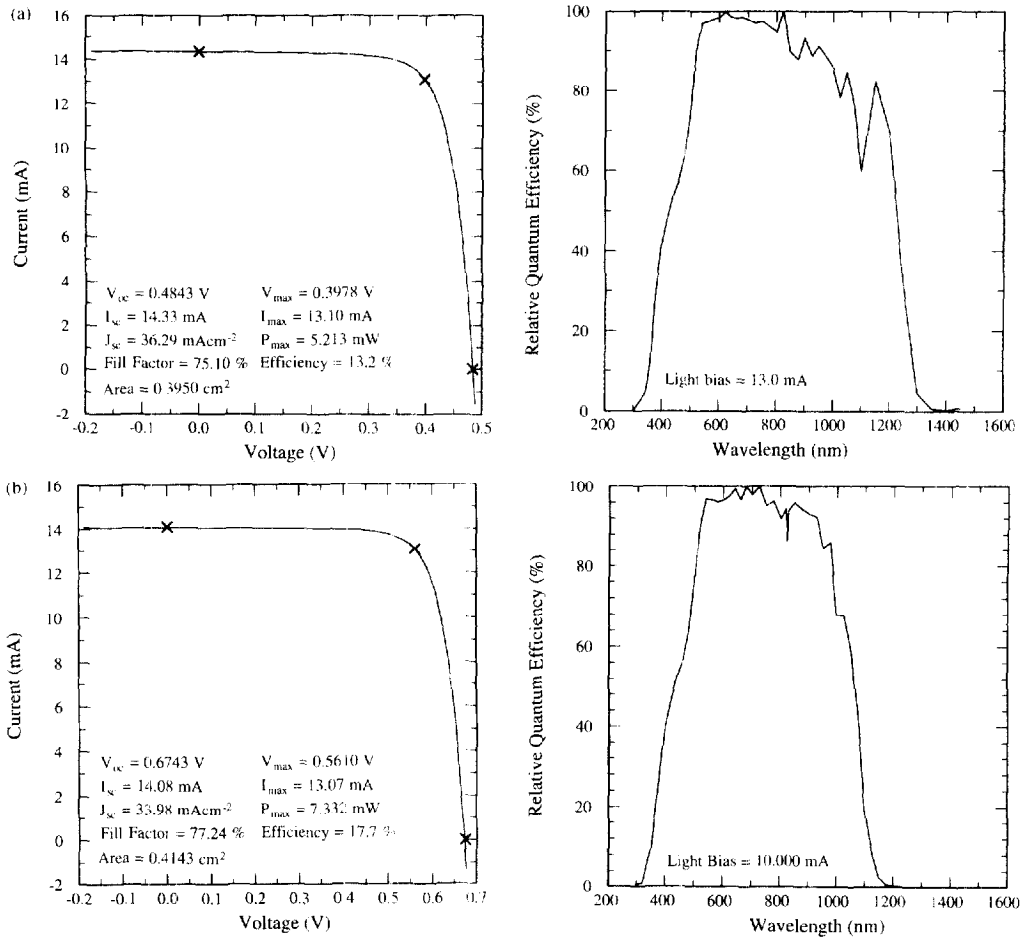


Fig. 22.  $\text{CuInSe}_2$ -based thin-film solar cells: (a) 13.2 %-efficiency  $\text{CuInSe}_2$  cell, (b) champion 17.7 %-efficient,  $\text{Cu(In,Ga)Se}_2$  cell. Light J-V and spectral response characteristics are presented for each.

*p-i-n* structure [296, 297], and Schottky barrier [298], indicative of the uncertainty of the exact cell operation, and perhaps the sensitivity of the cell operation to the deposition and processing approaches. Electron-beam induced-current (EBIC) measurements (light-biased and dark) of single-crystal and polycrystalline cell cross-sections have shown the presence of shallow and deep junctions [293, 299–301]. Other evidence based upon capacitance-voltage, spectral response, and bias-dependent spectral response argues for the existence of the heterojunction [301–304]. These seemingly contradictory results have not impeded the development of this polycrystalline technology into a precommercial phase. The danger of artifactual or measurement technique-induced error is possible with any of the ion or electron-based reports, which are common for the direct observation of the junction (electrical and metallurgical) location [304–308].

Certainly the positive and perhaps unique factors that favor this thin-film technology are stability and large-area production potential with performance characteristics similar to those for laboratory devices. The *stability* of this technology is represented by the data in

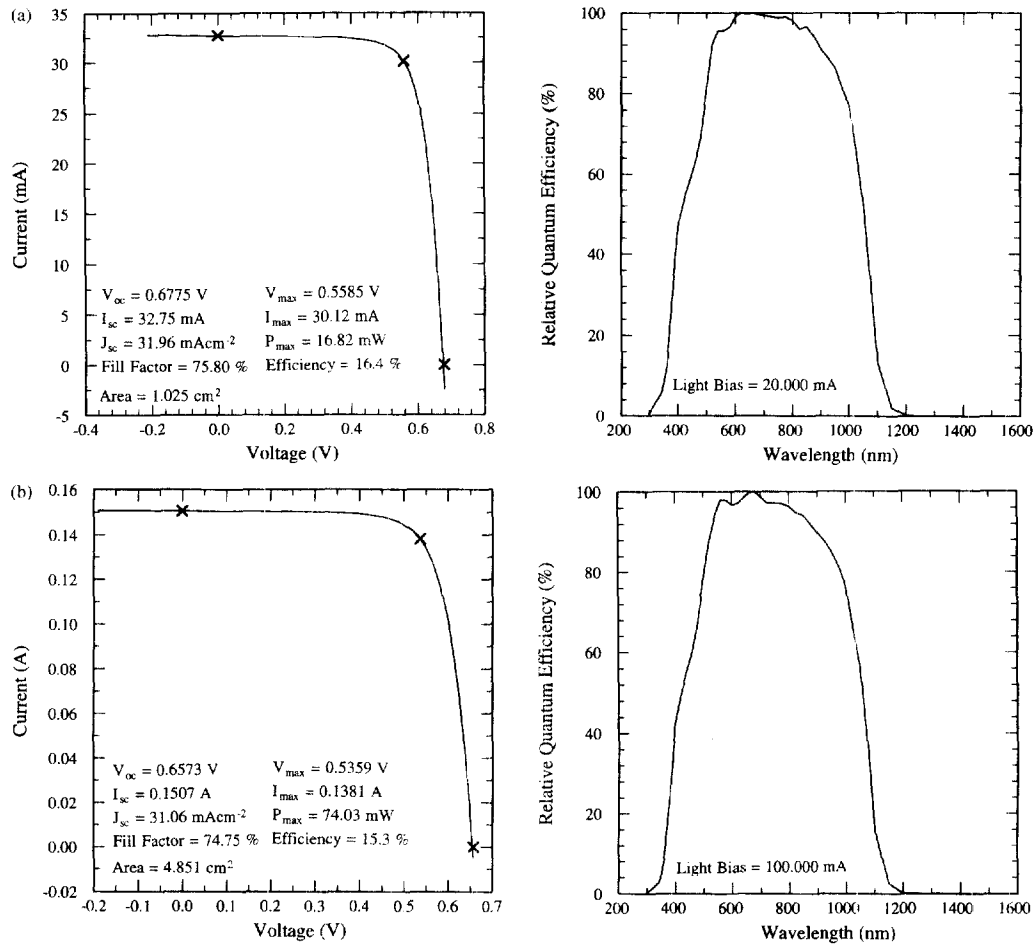


Fig. 23. Large-area Cu(In,Ga)Se<sub>2</sub> based cell, light I-V characteristics, indicating scalability of the process: (a) 1.025 cm<sup>2</sup> area, and (b) 4.851 cm<sup>2</sup> area.

Fig. 24 [309–314]. Both cells and modules have shown stable behavior, even after several thousand hours of outdoor and simulated light exposure. Such testing has been noted in both unencapsulated cells, as well as in encapsulated coupons, submodules, and modules. These data give evidence that this might be the most stable of the advanced technologies. The first- and second-generation modules have also passed a variety of qualification procedures, including those developed by Block V module acceptance under the U.S. DOE Large-Scale Array Program, and more recent industry and professional standards. The second positive indication for this thin-film technology is that it is possible to produce larger area devices (submodules and modules with areas in the 100–4000 cm<sup>2</sup> range) with efficiencies comparable to smaller area (1–10 cm<sup>2</sup>) cells [315]. This gives some confidence that the process is scaleable, i.e. is the performance of this technology is not limited to laboratory cells, but can be produced for commercial-scale components.

Another asset for this technology is the ability to produce device-quality CuInSe<sub>2</sub> by a variety of deposition techniques [316]. These are summarized in Table 5, and range from

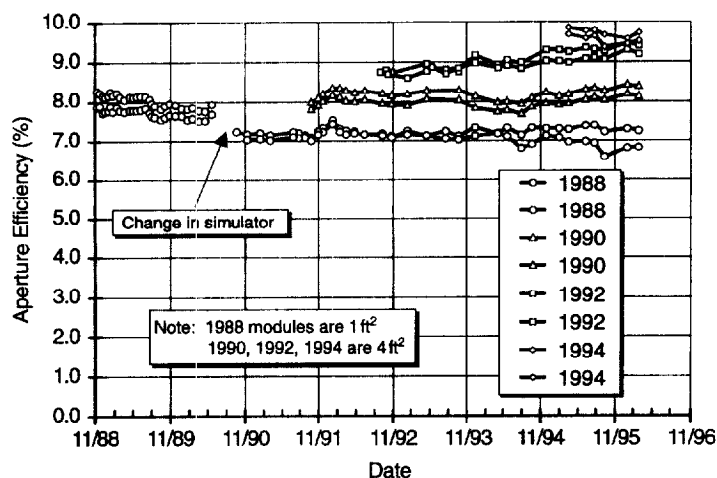


Fig. 24. Stability data on CuInSe<sub>2</sub>-based devices indicating reliability over extended period.

Table 5. Summary of deposition techniques used for research- and manufacturing-scale CuInSe<sub>2</sub>-based and CdTe-based thin-film materials and solar cells

Deposition technique	Research demonstration	Manufacturing demonstration
<i>CuInSe<sub>2</sub>-based devices</i>		
Flash evaporation	2.4% ; 1 cm <sup>2</sup>	
Two-source vacuum deposition	6.7% ; 1.02 cm <sup>2</sup>	
Three-source vacuum deposition	17.7% ; 0.4 cm <sup>2</sup>	9.1% ; 97 cm <sup>2</sup>
	15% ; 4 cm <sup>2</sup>	
Sputtering	4% ; 1.0 cm <sup>2</sup>	
Electron-beam evaporation or sputtering with selenization	14.1% ; 1 cm <sup>2</sup>	12.7% ; 69 cm <sup>2</sup>
		11% ; 3985 cm <sup>2</sup>
Electrodeposition	11.5% ; 0.99 cm <sup>2</sup>	
Molecular-beam epitaxy	3.6% ; 0.7 cm <sup>2</sup>	
Spray pyrolysis	2-3% ; 1 cm <sup>2</sup>	
<i>CdTe devices</i>		
Metal-organic CVD	11.9% ; 0.08 cm <sup>2</sup>	
Physical vapor deposition [PVD (vacuum)]	11.8% ; 0.3 cm <sup>2</sup>	
Atomic-layer epitaxy	14% ; 0.12 cm <sup>2</sup>	
Laser-assisted PVD	10.5% ; 0.10 cm <sup>2</sup>	
Molecular-beam epitaxy	10.5% ; 0.08 cm <sup>2</sup>	
Sputtering	10.4% ; 0.10 cm <sup>2</sup>	
AP CVD	9.9% ; 1.0 cm <sup>2</sup>	
Closed-spaced sublimation	15.8% ; 1.05 cm <sup>2</sup>	9.1% ; 7200 cm <sup>2</sup>
Screen printing	12.8% ; 0.8 cm <sup>2</sup>	8.7% ; 1200 cm <sup>2</sup>
Chemical spray deposition	14.8% ; 0.30 cm <sup>2</sup>	8.7% ; 3528 cm <sup>2</sup>
Electrodeposition	14.2% ; 0.02 cm <sup>2</sup>	8.4% ; 4540 cm <sup>2</sup>

vacuum-based (sputtering, resistive heating, electron-beam source) to non-vacuum (electroplating, chemical deposition, spraying) methods. It should be noted, however, that the highest efficiency cells have been produced by multiple-source, vacuum deposition of the ternary semiconductor. The economics of this approach have not been established, and a better basis for evaluating the cost effectiveness of this or other thin-film production approaches awaits data from pilot-plant or other commercial ventures. The early criticisms on the supply and costs for the indium (and gallium) have become less prevalent [317]. Indium is currently produced as a by-product of the zinc-refining process, and resources are estimated primarily from these values and not from other sources. Proponents of the In-based technologies point out that major fractions of energy production can be realized using In-based cells without requiring any other In sources or major decreases in costs [318]. The interface region between the window and the  $\text{Cu(In,Ga)Se}_2$  has been central to understanding and controlling the performance of higher efficiency cells. The contribution of an ordered defect chalcopyrite (ODC) at the very surface of the Cu-ternary alloy, first recognized and investigated by the EuroCIS research groups [261, 262, 266], was to the understanding of the definition of the electrical junction. This ODC has been identified in a number of studies, and its presence is considered by some groups as an essential component of the device-interface structure. It was the identification and understanding of these growth processes that led NREL to the development of the exceptional performance levels for the current solar cells [263, 264]—now by several different fabrication techniques. Device-quality absorber films require two seemingly contrary properties: Cu-rich layers to produce both adequate morphology and electrical properties, and a Cu-poor surface layer to realize a high-performance junction. This requires careful engineering of the film during growth or post-deposition processing. The Cu-rich region is gained simply by increasing the Cu flux or incorporation during film growth. The most common technique is to deposit the film at about 550 °C, at which temperature the CuSe phase melts and acts as a flux solute while being consumed. With the addition of In, the desired surface layer (Cu-poor) can then be attained. Several other processes have been shown to be successful. Figure 25 summarizes chemical reaction paths to realizing device-quality absorbers. Of course, each of these approaches has issues relating to the transfer to manufacturing, and these are also summarized in this representation. A major point of Fig. 25 is that the important factor in processing the complex absorber is the chemical reaction path, and *not* the technique used in producing the film. Whether vacuum deposition or electroplating, control of the film chemical structure is the important issue, and the reaction paths outlined in Fig. 25 govern the yield of high-performance devices [323].

Interesting to the development and understanding of the  $\text{CuInSe}_2$ -based device is the importance of the substrate. The first cells were on metal-coated borosilicate glass and polished ceramics [249, 250, 259, 260]. Higher cell efficiencies evolved on soda-lime glasses, used primarily for cost arguments. Initial considerations of the substrate focused on the importance of the Sn-rich or deficient sides of the float-glass itself [324]. Sodium was detected in the better devices, and correlations were made between the presence and concentrations of Na, the possible origin from the glass substrate, and the cell performance [325–328]. The role of Na in these films has not been completely explained, but it is now considered as a “required impurity” in most device-quality absorbers [327]. It is observed that Na in the  $\text{Cu(In,Ga)Se}_2$  layer leads to a strong (112)-preferred film orientation, conducive from early structural studies to better device performance. Initial results have also indicated the generation of a shallow acceptor state about 75 eV above the valence band

Pictorial Description Start      --->      Finish	Chemical Reaction Path	Manufacturing Issues
(1) 17.1% - Concurrent delivery of the metals in the presence of Se (2-stage)		
	<ul style="list-style-type: none"> <li><math>\text{Cu} + (\text{In,Ga}) + \text{Se} \xrightarrow{500^\circ\text{C}} \text{Cu(In,Ga)Se}_2 + \text{Cu}_2\text{Se}</math></li> <li>CIGS: <math>\text{Cu}_2\text{Se} + (\text{In,Ga}) + \text{Se} \xrightarrow{550^\circ\text{C}} \text{Cu(In,Ga)Se}_2</math></li> </ul>	<ul style="list-style-type: none"> <li>Stage 1 Cu-rich precursor can be easily synthesized</li> <li>Stage 2 conversion does not require Cu</li> </ul>
(2) 16.8% - Sequential delivery of Metals in the presence of Se (3-stage)		
	<ul style="list-style-type: none"> <li><math>(\text{In,Ga})\text{Se}_x + \text{Cu}_2\text{Se} + \text{Se} \xrightarrow{500^\circ\text{C}} \text{Cu(In,Ga)Se}_2 + \text{Cu}_2\text{Se}</math></li> <li>CIGS: <math>\text{Cu}_2\text{Se} + (\text{In,Ga}) + \text{Se} \xrightarrow{550^\circ\text{C}} \text{Cu(In,Ga)Se}_2</math></li> </ul>	<ul style="list-style-type: none"> <li>Separates Cu &amp; (In,Ga) delivery</li> <li>Simplifies in-situ process control</li> <li>Conducive to large-area deposition technology</li> </ul>
(3) 15.1% - In-line / Variable Flux Process (1-stage)		
	<ul style="list-style-type: none"> <li><math>\text{Cu} + (\text{In,Ga}) + \text{Se} \xrightarrow{500^\circ\text{C}} \text{Cu(In,Ga)Se}_2 + \text{Cu}_2\text{Se}</math></li> <li>CIGS: <math>\text{Cu}_2\text{Se} + \text{Cu} + (\text{In,Ga}) + \text{Se} \xrightarrow{550^\circ\text{C}} \text{Cu(In,Ga)Se}_2</math></li> </ul>	<ul style="list-style-type: none"> <li>Designed for in-line, continuous large-area deposition</li> <li>Process design flexibility</li> </ul>
(4) 12.6% - Sequential delivery of metals without Se followed by compound formation in Se vapor (2-3 stages)		
	<ul style="list-style-type: none"> <li><math>\text{Cu}_x\text{In} + \text{Cu}_y\text{Ga} \rightarrow \text{Cu}_x\text{In} + \text{Cu}_y\text{Ga} + \text{Cu} + \text{In} + \text{Se} \xrightarrow{300^\circ\text{C}} \text{Cu}_2\text{Se} + (\text{In,Ga})_2\text{Se}_3 + \text{Se}</math></li> <li><math>\xrightarrow{450^\circ\text{C}} \text{Cu(In,Ga)Se}_2</math></li> </ul>	<ul style="list-style-type: none"> <li>Separates deposition processes from thermal/chemical processes</li> <li>Utilizes established large-area metal deposition technology</li> </ul>

Fig. 25. Chemical reaction paths to realizing device-quality  $\text{CuInSe}_2$ -based absorbers, indicating that any deposition method can be tailored to produce high-efficiency cells.

associated with the Na in the doubly-charged  $\text{Cu(In,Ga)Se}_3$ , increasing the free-carrier concentration [326]. The acceptable (perhaps optimal) concentrations have been identified, and some cell producers introduce Na in addition to that available in the substrate to improve cell performance [327, 328]. Sodium has been purposely placed in the ternary alloy during vapor growth, by post-deposition diffusion, and by ion implantation [325–328]. The segregation, diffusion, and addition of the Na has been investigated, but the exact mechanisms of incorporation and the correlation to the electro-optical and structural characteristics remain valid areas of study. The soda-lime glass substrate provides economic advantages for this technology, but it is apparent that it also has contributed unknowingly to the early performance development of this thin-film cell.

The low  $V_{oc}$  has prompted investigating methods of engineering the material to provide better interface properties [285, 329–331]. Other window semiconductors, such as ZnO, have shown promise [332–335]. The production of efficient devices has been tied closely with the use of the CdS-based window. In fact, the concern with the window has impact and interest in minimizing another area of concern for these technologies—the environment [336]. Cadmium certainly raises apprehension for consumers, and a host of studies continues to evaluate the problems associated with this and other potentially dangerous materials being pursued in various PV technologies. (Environmental aspects are addressed in more detail later in this review.) The thickness of the CdS layer has been minimized in this device by the use of thinner CdS films. Currently, about 200–500 Å is used in high-efficiency cells. The CdS is deposited by chemical bath deposition [337], which also provides for conformal

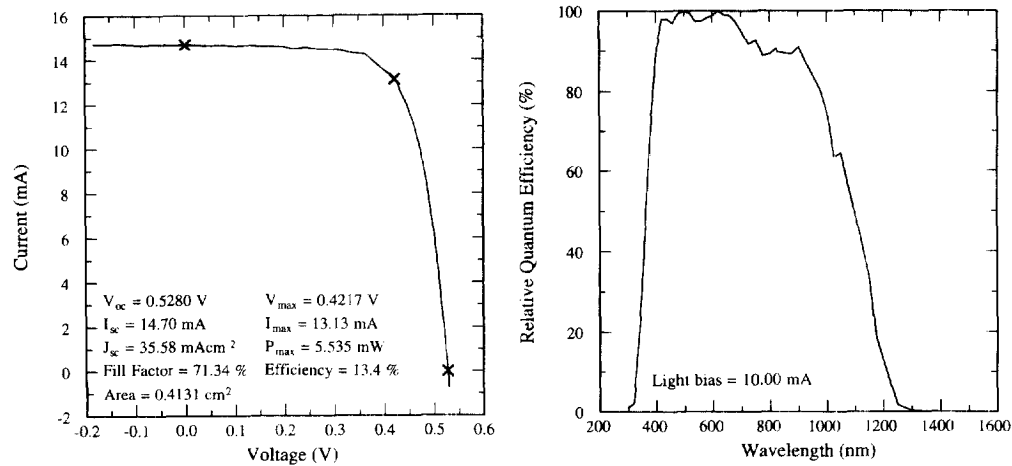


Fig. 26. High-performance cells using only the ZnO window : (a)  $I$ - $V$  characteristics ; and (b) spectral response.

coverage of the absorber semiconductor. Another benefit of the thin CdS is the improvement in the spectral response of the devices, which are no longer limited by the absorption edge of the CdS [263, 323]. However, the complete elimination of the CdS is viewed as a major contribution to reducing cost (fewer processing steps), complexity (less complex design consideration), and negative environmental technology perception. Recently, high-performance cells using only the ZnO window have been reported, and one is represented with the  $I$ - $V$  characteristics of Fig. 26 [335]. It has to be acknowledged that the elimination of the Cd does not make this thin-film technology one that is universally accepted as “green”—the Se and Ga do have some toxicity problems [see Refs 386–388]. However, these are being studied to ensure that no technology is produced that poses an environmental threat, and certainly the initial data support the relative benignity of this Cu-ternary approach.

Other Cu-ternaries are also undergoing research and development (see Table 6). The (Cd,Zn)S/CuGaSe<sub>2</sub> thin-film cell has exceeded 10% [338]. This approach features a higher  $V_{oc}$  device, and the elimination of the In. (Gallium has about the same abundance as cadmium, but its availability may be of concern.) CuInS<sub>2</sub> offers an almost ideal bandgap (1.54 eV) for terrestrial applications, but lacked substantial development efforts owing to problems in controlling the sulfur during growth. Thin-film cells have now been produced with efficiencies in the 10% range, and interest continues in both research and industrial laboratories [339, 340].

#### ISSUES AND CONCERNS—CuInSe<sub>2</sub> AND ALLOYS:

- **Research:** This technology remains rich in its research opportunities. The chemical reaction paths have been identified, but not refined for all film production approaches. The elimination of the CdS is of importance, and the realization of alternatives to this heterojunction partner will enhance the technology acceptance. Other research areas include: (1) process development aimed at scale-up of demonstrated high-efficiency devices; (2) understanding and identification of the

Table 6. Summary of confirmed Cu-ternary and multinary solar-cell efficiencies and related parameters. Data are presented for various cells to give indications of improvements and scope of device developments. Measurements were performed under 25°C, 1000 W/m<sup>2</sup>, ASTM E892 global conditions unless otherwise noted. The area definition used for non-concentrator cells is total area. The independently confirmed efficiencies in this table are from other standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Organization	Comments
<i>One sun cells</i>							
6/88	2.400	464	38.5	65.4	11.7	ARCO Solar	ZnO/[Cd,Zn]S/ CuInSe <sub>2</sub>
11/92	0.192	539	33.7	73.6	13.4	Siemens Solar	ZnO/CdS/CuIn Se + (I-II-VI <sub>2</sub> ) multinary/Mo
12/86	1.074	509	30.4	66	10.2	Boeing	CdS/CuInSe <sub>2</sub>
6/93	1.003	604	34.3	67.9	14.1	Boeing	ZnO/[Cd,Zn]S/ Cu(In,Ga)Se <sub>2</sub>
9/87	1.028	445	35	64.6	10.1	IEC	ZnO/[Cd,Zn]S/ CuInSe <sub>2</sub>
1/91	0.99	483	35.6	66.7	11.5	ISET	ZnO/[Cd,Zn]S/ CuInSe <sub>2</sub> /Mo/glass
3/96	0.41	674	34	77.3	17.7	NREL	MgF <sub>2</sub> /ZnO/CdS/Cu (In,Ga)Se <sub>2</sub> /Mo/glass
11/94	1.03	678	32	75.8	16.4	NREL	MgF <sub>2</sub> /ZnO/CdS/Cu (In,Ga)Se <sub>2</sub> /Mo/glass
11/94	0.41	594	32.8	73.8	14.4	Solarex	CdS/Cu(In,Ga)Se <sub>2</sub> / Mo/glass

minority-carrier properties in relation to materials properties and junction characteristics; (3) development (refinement) of device models that can be utilized in directing research and manufacturing (analogous to the successful ones used for a-Si:H cells); (4) investigation and development of the contacts to both front and back surfaces. Molybdenum is the back contact of choice, but its role and alternatives (lower cost) are not well known; (5) sodium: what is the role of Na in these films? Some initial suggestions have been reported (e.g. verification of acceptable concentrations), but the control and advantage of this element in the Cu-multinary are not finalized. The soda-lime glass substrate provides economic and property advantages, but the exact mechanisms of Na incorporation and effects on electro-optical and perhaps structural characteristics remains a valid area of investigation.

- **Complexity:** Cu(In,Ga)(S,Se)<sub>2</sub> is a semiconducting absorber that offers extraordinary flexibility for device engineering. It also is complex for both material control and related manufacturing cost. The former issue seems to have been shown to be less important with modules produced having efficiencies comparable to the better small-area cells. However, the fact that marketable product has not appeared may be an indication that the predicted cost advantage over crystalline-Si competition has not been attained—perhaps because of the adverse effect of “complexity” on manufacturing cost.
- **Stability:** Yes, this has been touted as “...the most stable of the thin-film alternatives”—with justification. However, one issue of stability should be acknowledged.

The cell performance does change under light exposure. Efficiencies tend to *rise* by 2–10% under the first 10–30 min of exposure of light. (Almost all champion cells are reported after such light soaking.) Albeit a more advantageous change than for a-Si:H, it is still a *change* in performance. The ZnO has some sensitivity to humidity, and module design has to consider this.

- **Device issues:** The Cu-ternary of multinary solar cell has an inherent low bandgap. This semiconductor provides some issues for module manufacturing and deployment: (1) the low  $V_{oc}$  and high  $J_{sc}$  are parameters that complicate module design. (System engineers, in general, prefer high-voltage, lower current devices.) And, (2) the low bandgap means that the modules lose about 20% performance output under normal operating conditions (temperature). Higher Ga use is expected to ameliorate these issues.
- **Scale-up:** Module performance and cell performance differ by a wider margin than for other technologies. It is uncertain whether the high-performance processes used in producing laboratory cells can be implemented in a large-scale manufacturing environment with adequate yields.
- **Manufacturing base:** The industry and manufacturing options are still immature and unproved. In 1988, ARCO Solar indicated that it would introduce product within a year. This has not happened (perhaps for reasons cited above), and the list of commercial interests in this technology has not escalated significantly. The technology is in some need of introducing a viable product into the marketplace, or there may be loss of confidence that this semiconductor option can actually compete. This may call for additional funding help from government sectors to help infant industry bridge the gap between research prototypes and useful commercial products.

### 5.2. Cadmium telluride

Since the 1960s, CdTe has been a candidate photovoltaic material, with periodic waning and growing interest in its viability [341–347]. Various materials and device issues have interrupted its development during this extended period, and again recently this cell has re-emerged as a major thin-film approach, thanks to the tenacity and cleverness of research and industry teams. Its 1.5 eV bandgap is well matched to the terrestrial spectrum, and direct-gap transition results in high absorption over the solar spectrum –but difficulties with reliable electrical contacts (especially to the *p*-type material) [348, 349], control and understanding of the electrical properties (including doping and tendency to be semi-insulating), environmental concerns (cadmium), and the sensitivity of the cell to the environment (e.g. water vapor effects) have limited the commercial interest and market introduction. Although it is limited to a superstrate configuration with high-processing temperatures (i.e.  $\geq 55^\circ\text{C}$ ), large-area modules with greater than 9% efficiency and low-temperature coefficients have been manufactured. Recent progress in materials development and device design have contributed to a significant resurgence of this polycrystalline thin-film technology [350–352].

First suggestions of CdTe as a photovoltaic material were made by Rappaport, based upon his predictions of optimum bandgap for solar conditions [353]. The first efficient polycrystalline, thin-film cells were reported by Cusano *et al.*, using *p*-Cu<sub>2</sub>-Te/*n*-CdTe structures [354]. The first thin-film heterojunctions, evaporated undoped CdTe on CdS/SnO<sub>2</sub>/glass structures, appeared in 1969 [355]. The initial CdS/CdTe thin-film device



is attributed to Bonnet, who fabricated 5% cells using an evaporated CdS on a CdTe film [356]. Much of the pioneering work with CdTe was accomplished on single crystals [357–359]. This approach laid the foundation to understanding the thin-film device because many analogies exist between the bulk crystalline and thin polycrystalline materials. This approach distinguished the development of this technology from CuInSe<sub>2</sub>. Although some thin-film material and device research was conducted, the strength of this early work was to provide sound technical information on which further device development could proceed. Attention was directed toward thin layers when screen-printed and sintered CdTe cells were reported with >10% efficiencies by Matsushita [360]. This led to the commercialization of this product, with 500 cm<sup>2</sup> submodules having >6% conversion efficiencies—and the application to power calculators. Close-space vapor transport deposition was used to produce small-area cells with very high efficiencies by Tyan and co-workers [361–363]. Basol *et al.* reported the first confirmed thin-film CdS/CdTe and CdS/Hg<sub>0.15</sub>Cd<sub>0.85</sub>Te (with  $x < 0.15$  to decrease bandgap (increase current density), lower resistivity, and assist in contacting) with efficiencies of 9.4% and 10.1%, respectively, for 4 cm<sup>2</sup> [364]. A number of other significant cell efficiencies were reported during this period, including a 4 cm<sup>2</sup> SnO<sub>2</sub>/CdTe device with 10.5% efficiency by Arco Solar [365]. Ametek developed a 1 cm<sup>2</sup>, 11% electrodeposited device that incorporated a ZnTe layer in the *p*-layer contacting process [366]. These important technology demonstrations, however, provided little or no information about cell stability.

Over this period, Chu *et al.* continued to develop close-space vapor deposition, and reported a progression of cells in the 10–13% range [367–369]. A significant and singular contribution to the CdTe thin-film PV technology came in 1992, when an extraordinary set of cells were confirmed with efficiencies exceeding 15%. The best of these devices (or any CdTe thin-film cell), produced by Ferekides and Britt [370], is the 15.8% cell (1 cm<sup>2</sup> area, borosilicate glass substrate) shown in Fig. 27. This champion cell (CdTe grown by the close-space vapor method) provided an unprecedented technological leap and a target for other research groups. The substrate was more expensive 7059 glass, but the accomplishment brought some focus to processing on soda-lime glass at lower temperatures (<550 °C)—and several groups have produced cells in the 12–15% range on this less-

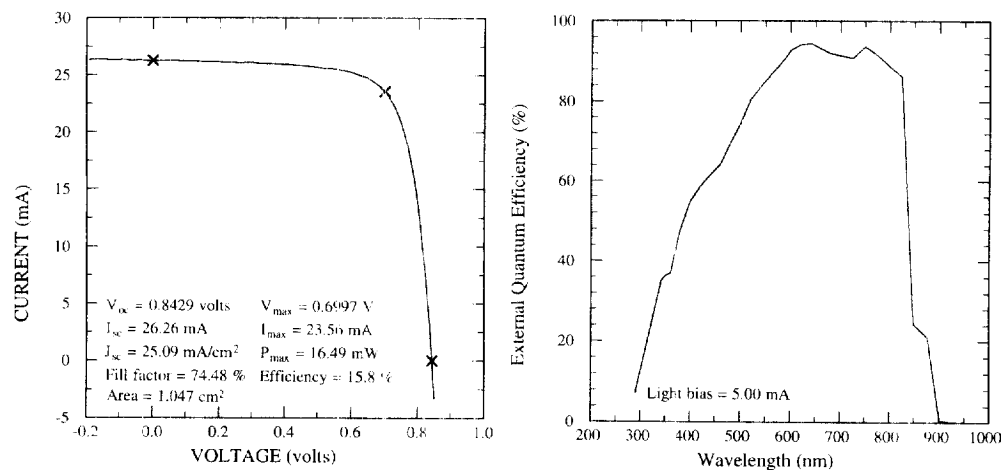


Fig. 27. 15.8 % CdTe thin-film solar cell: (a) I-V characteristic; and (b) spectral response.

expensive substrate [371–374]. (The sodium-containing substrates provide some benefit for the Cu-ternaries which seem to improve with Na content, but in contrast the Na is a minority-carrier lifetime killer in the CdTe. Comparable cells to the 15.8% device, but deposited on soda-lime glass, reached 14.2% by the same research team using the same deposition method [375].) Although efficiency continued to improve throughout the CdTe thin-film cell community [376–378], this record remains intact. The best cell using a soda-lime glass substrate was recently confirmed at 14.7% for a small-area cell by Kester [379]. This cell had no antireflection coating and was deposited on a non-optimal, 5-mm thick glass, having some significant additional light absorption over the normal substrate. The light  $I$ - $V$  characteristics and spectral response data for this device are shown in Fig. 28. The cell was produced by spray deposition of the CdTe, using a much-refined and potentially inexpensive Golden Photon technology. This cell shows that quality CdTe material can be fabricated by production approaches. However, questions of control over large areas, manufacturing-line yields, and continuous processing are still issues for commercial phases. Table 7 provides a summary of NREL-confirmed performance parameters for a number of CdTe thin-film solar cells.

Most of the higher efficiency cells involve a chemical treatment in  $\text{CdCl}_2$ : methanol solutions at high temperatures ( $\sim 400^\circ\text{C}$ ) [380–382]. The beneficial effects of this processing have been attributed to enhanced grain size (grain growth), densification, evolution of a  $p$ - $i$ - $n$  or heterojunction, surface passivation (including grain boundaries), alteration of shallow and/or deep electronic levels due to Cd and/or Cl incorporation, improvement in morphology, and the formation of an interfacial  $\text{CdS}_{1-x}\text{Te}_x$  layer by interdiffusion of related physicochemical process [383–385]. Although changes in a number of macroscale electro-optical properties have been associated with this processing, the exact mechanisms governing the performance improvement have not been universally or generally identified. The optimal conditions for processing are known to the cell producers, and it appears that an ensemble of co-interacting and independent effects are involved during this chemical and thermal processing that result in enhanced cell performance. This remains an area of research interest for these compound semiconductor cells.

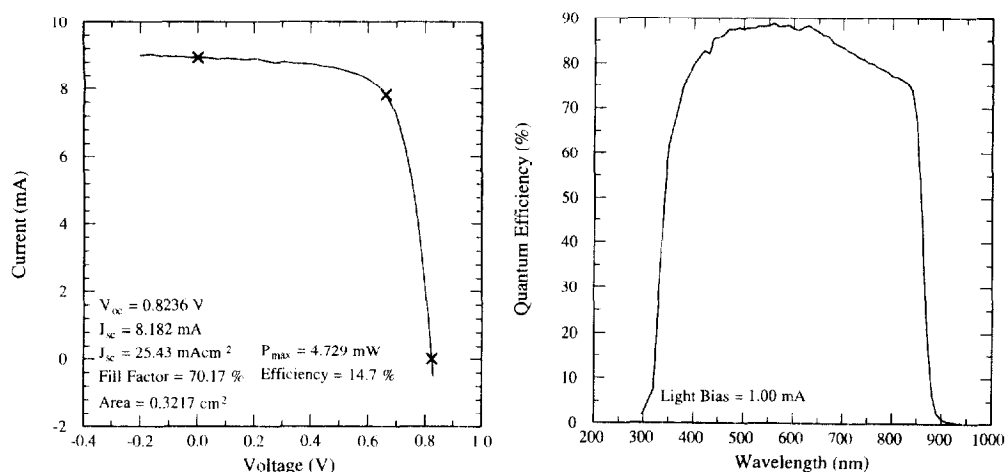


Fig. 28. 14.7% CdTe thin-film solar cell on soda-lime glass substrate: (a)  $I$ - $V$  characteristics; and (b) spectral response.

Table 7. Summary of confirmed thin-film polycrystalline CdTe solar-cell efficiencies and related parameters. Data are presented for various cells to give indications of improvements and scope of device development. Measurements were performed under 25°C, 100 W/m<sup>2</sup>, ASTM E892 global conditions unless otherwise noted. The area definition used for non-concentrator cells is total area. The independently confirmed efficiencies in this table are from standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Organization	Comments
<i>One sun cells</i>							
10/91	0.191	790	20.10	69.4	11.0	IEC	Glass/ITO/CdS/ CdTe/Cu/Au
7/95	0.824	840	20.66	74.0	12.8	NREL	Glass/SnO <sub>2</sub> /CdS/CdTe
5/89	0.313	783	24.98	62.7	12.3	Photon Energy	Glass/SnO <sub>2</sub> /CdS/CdTe
5/91	0.300	788	26.18	61.4	12.7	Photon Energy	Glass/SnO <sub>2</sub> /CdS/CdTe
4/88	1.022	736	21.90	65.7	10.6	SMU	Glass/SnO <sub>2</sub> /CdS/ CdTe/HgTeGa
6/92	1.047	843	25.09	74.5	15.8	Univ. South Florida	MgF <sub>2</sub> /7059 glass/SnO <sub>2</sub> /CdS/ CdTe/C/Ag
10/89	1.068	767	20.93	69.6	11.2	AMETEK	Glass/SnO <sub>2</sub> /CdS/ CdTe/ZnTe/Ni
6/91	0.080	745	22.10	66.0	10.9	Georgia Tech	Glass/SnO <sub>2</sub> /CdS/ MOCVD CdTe
4/95	1.115	828	20.90	74.6	12.9	Solar Cells, Inc.	MgF <sub>2</sub> /glass/SnO <sub>2</sub> / CdS/CdTe
11/92	0.114	815	17.61	72.8	10.4	Univ. Toledo	Glass/SnO <sub>2</sub> /CdS/ sputtered CdTe/Cu/Au

Two areas that concern this cell relate to contracting. The first is the transparent conducting oxide (TCO), typically SnO<sub>2</sub> or ITO, that provides the electrical contact to the window-layer semiconductor. The constraints are to have this film highly conductive ( $< 10 \Omega/\square$ ), optically transparent ( $> 80\%$ ) over 350–900 nm wavelengths, and with low surface roughness (conducive to patterning and subsequent layer growth). These layers are deposited by sputtering, CVD or spray pyrolysis. Alternatives have been under development and consideration—with the ramifications of better TCOs important for other thin-film technologies as well. One alternative, developed for CdTe by Sheldon and co-workers, is Cd<sub>2</sub>SnO<sub>4</sub>, which has demonstrated both improved conductivities (with carrier concentrations nearly  $10^{21} \text{ cm}^{-3}$  and sheet resistances of  $\sim 2.5 \Omega/\square$ ) and better transmission than SnO<sub>2</sub> [377]. Atomic-force microscopy investigations have shown lower surface roughness compared to either SnO<sub>2</sub> or ITO. The second is the back-contact issue. Common contacts include HgTe- or Cu-doped graphite (applied as a paste), Cu-doped ZnTe, and Te with a metal overlayer. Recent attention has been with ZnTe-based contacts deposited by a dry process at low temperatures ( $\sim 300^\circ \text{C}$ ). The importance is that this contact, whether a single layer ZnTe: Cu/Ni or an improved bilayer ZnTe: CuNi, can be incorporated easily into the device manufacturing, while enabling low-contact resistance ( $0.15 \Omega \text{ cm}^2$ ) and relatively good stability [377].

The manufacturing of products for the energy production market is still in its infancy,

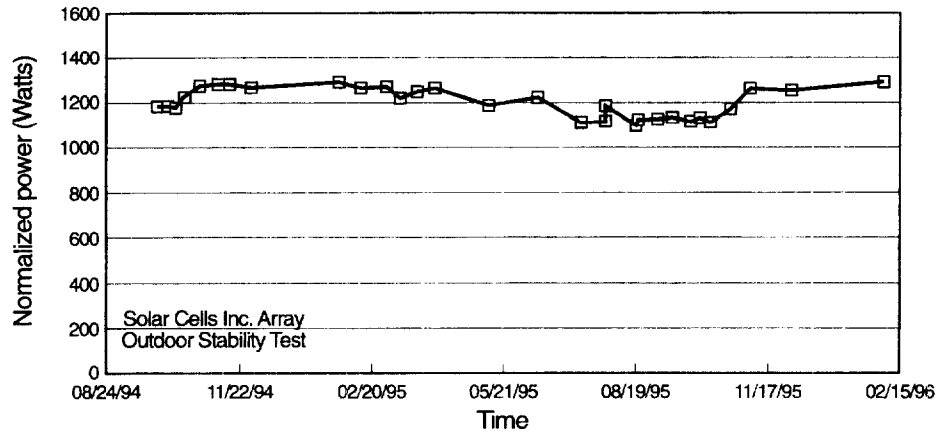


Fig. 29. Stability data for CdTe module produced by Solar Cells Inc., indicating power output stability over 2 year period.

although Solar Cells, Inc. has produced 9.1%, >60 W modules, with >100 kW of this product in field testing. Stability data for a representative CdTe module are shown in Fig. 29. With adequate packaging, humidity/water intrusion in modules is minimized (a stress that is associated with contact oxidation and failure and other degradation mechanisms with this technology). At the time of writing, two major CdTe thin-film solar cell manufacturers are preparing for sales, and a third effort has been announced for start-up in early 1998. An important inhibition to the more rapid deployment of CdTe as a terrestrial PV option is concerned with the environmental impact of this cell type, and to a lesser degree, the CdS/Cu(In,Ga)Se<sub>2</sub> cell [335, 386-389]. (This had led to more limited funding for CdTe thin-film photovoltaics in the European Communities, although the recent announcement of a manufacturing effort in Germany gives some sign that some of the environmental road-blocks have been lifted.) The Cd (in both the CdTe and the CdS layers) is the primary consideration. Modules have undergone extensive testing for fire and leaching, as well as potential mechanisms for recycling, and disposal. The results are generally positive for minimal impact on the environment, but some significant areas of concern have been exposed. The reader is directed to the studies reported in the literature [377-380]. These concerns are being carefully addressed by the manufacturing and PV research communities. The cadmium issue is currently localized with PV and environmental groups; however, some level of confidence has to be gained to ensure consumer acceptance.

#### ISSUES AND CONCERNS: CdTe

- Research: Several issues remain on the research side, including: (1) process development aimed at scale-up of demonstrated high-efficiency devices (analogous to other polycrystalline film technologies); (2) adequate device models guiding device and process development; (3) control, engineering, and optimization of the CdS/CdTe interface, and (4) continued improvement of the contact to the *p*-type layer and understanding of the mechanisms that cause changes in the contact properties. Inherent to the materials work is the understanding and identification of the physical.

structural, chemical, and electro-optical effects of the  $\text{CdCl}_2$ -processing step, so important to the realization of high-performance devices. (This includes the continued identification of alternatives that might be more satisfactory to incorporation into a manufacturing operation.) Some additional efforts should be expended in the analysis portions relating to this technology—especially in the refinement of current measurement techniques and development of new methods to give insight into the interface properties and changes: (5) role of oxygen: gain enhancement, defect annihilation, doping effects.

- **Substrates:** The best performances have been produced on high-quality and higher cost borosilicate glasses. Sodium may have adverse effects on CdTe (although some researchers report to the contrary), and soda-lime glasses, for example, are more difficult to incorporate in the cell design. The identification and use of lower cost substrates to produce high-performance devices would benefit the economics of this technology (although not a driver). The role of Na must be better understood.
- **Cadmium:** Although relatively little Cd is used in the module, it is an irreplaceable part of this cell technology, and is of concern to health agencies and policy makers. The major concern is whether commercial CdTe modules will be classified as a hazardous waste, based upon initial testing by government and independent agencies. Cost effectiveness of recycling of the Cd from waste module can also adversely affect the product cost. The environmental concerns seem to be limiting investment in this technology path.
- **Stability:** Although many cells and modules have shown stabilized characteristics, others have not. The mechanisms of degradation have not been fully identified or examined because of the infancy of the product development. Copper diffusion, contact oxidation and other contact degradation in the device, and humidity/water intrusion in modules remain major questions.
- **Scale-up:** Module performance and cell performance differ by a wider margin than for other technologies. The paths to incorporate the high-performance processes used in producing laboratory cells in a large-scale manufacturing environment with adequate yields are not fully defined. It should also be pointed out that four different deposition technologies have been used to demonstrate scale-up potential for larger area cells and modules.
- **Manufacturing base:** The industry and manufacturing options are immature and unproved. Although more than 10 deposition methods have produced > 10% devices, none has emerged as “the” low-cost approach. Processes that should be low cost have led to 9% module efficiencies. Each current manufacturing unit uses a different, but potentially inexpensive, approach (evaporation, spraying, screen printing/sintering, and electrodeposition)—a partial indication of the uncertainty of direction (although this can be reviewed as a strength of versatility and less problematic for patent considerations). At a time when thin-film technologies need industry stabilization and expansion, one major thin-film CdTe manufacturer recently dropped its operations.

## 6. AMORPHOUS THIN FILMS

In contrast to more perfect crystalline materials, amorphous semiconductors have neither short- nor long-range structural order. The first suggestions for using these “structureless”

materials in device applications came in 1938 when Carlson introduced them for the Xerography process [390]. Switching phenomena in amorphous chalcogenide glasses was discovered by Ovshinsky in 1958 [391–393]. Photoconductivity in amorphous Si produced by silane discharge was first investigated by Chittick *et al.* [394]. This work established that the material differed electro-optically from that produced by evaporation or sputtering. The explanation of the role of hydrogen in this semiconductor was given by Lewis *et al.* [395]. The compensation of dangling Si bonds was shown to reduce the density of gap states in the a-Si:H alloy over its unhydrogenated analogue. Although most device research groups had used silane discharge methods to produce semiconducting amorphous Si, there was a reluctance to acknowledge that the amorphous Si material incorporated appreciable amounts of hydrogen. Triska *et al.* [396] were among the first to show that discharge-produced amorphous Si contained substantial hydrogen concentrations—later quantified to be in the 10–40% range and mostly bonded to the Si atoms. In fact, the bandgap of the material can be controlled by the amount of hydrogen incorporated—a fact that enhances this semiconductor's applicability and versatility in photovoltaics. The demonstration of controlled *n*- or *p*-type doping of a-Si:H by Spear and LeComber [397–399] was an important advancement for electronic applications. The first solar cells using a-Si:H were fabricated in 1974, and the report of a 5.5% Schottky barrier cell (with 0.07 cm<sup>2</sup> area) by Carlson and Wronski [400] established a viable new field of R&D for the photovoltaic community. Since then, the amorphous Si:H market has thrived, building experience initially in utilizing the cells to power consumer products (such as calculators and watches) and expanding to planned 10 MW per year production facilities aimed at power generation for both utility and decentralized applications.

#### 6.1. Amorphous Si:H cells

At its introduction, a-Si:H seemed to be the ideal photovoltaic candidate. Its native bandgap of  $\sim 1.7$  eV could be varied over tenths of eVs by changing the hydrogen content and established the physics of this semiconductor to be different than that of crystalline Si. Its absorption characteristics (Fig. 30) validated the material's economy with only 1/100 of the thickness needed to absorb the same amount of sunlight as its single-crystal relative. This thin film could be deposited on inexpensive substrates in any dimension for large-scale production. It had spin-offs to other electronic technologies (transistors, flat-panel displays, detectors) that enhanced its scientific interest, investigation and development. For PV, however, it has one concern—that of instabilities observed when exposed to light (the Staebler–Wronski Effect [401, 402]); a concern that has certainly slowed a more rapid deployment as a power-generating technology.

The evolution of amorphous cell efficiencies, presented graphically in Fig. 31, mirrors that of the polycrystalline devices. Since their first reports in about 1975, the performance of research cells has improved steadily from about 2.5% to above 12% [403–405]. Some additional care (beyond area definitions and related conditions) must be taken in interpreting and comparing efficiency reports during this period. Because of the changes in performance after exposure to light, many of the efficiencies for devices have been reported as “initial”—or those measured *before* any light-induced changes. Since many effects can contribute to the change in efficiency, only the highest efficiencies have traditionally been reported. It is true that many >10% amorphous cells have been realized, but relatively few (if any) are confirmed at the same efficiency after some hours of operation. Several international intercomparisons have validated these stability concerns [37, 38]. The problem

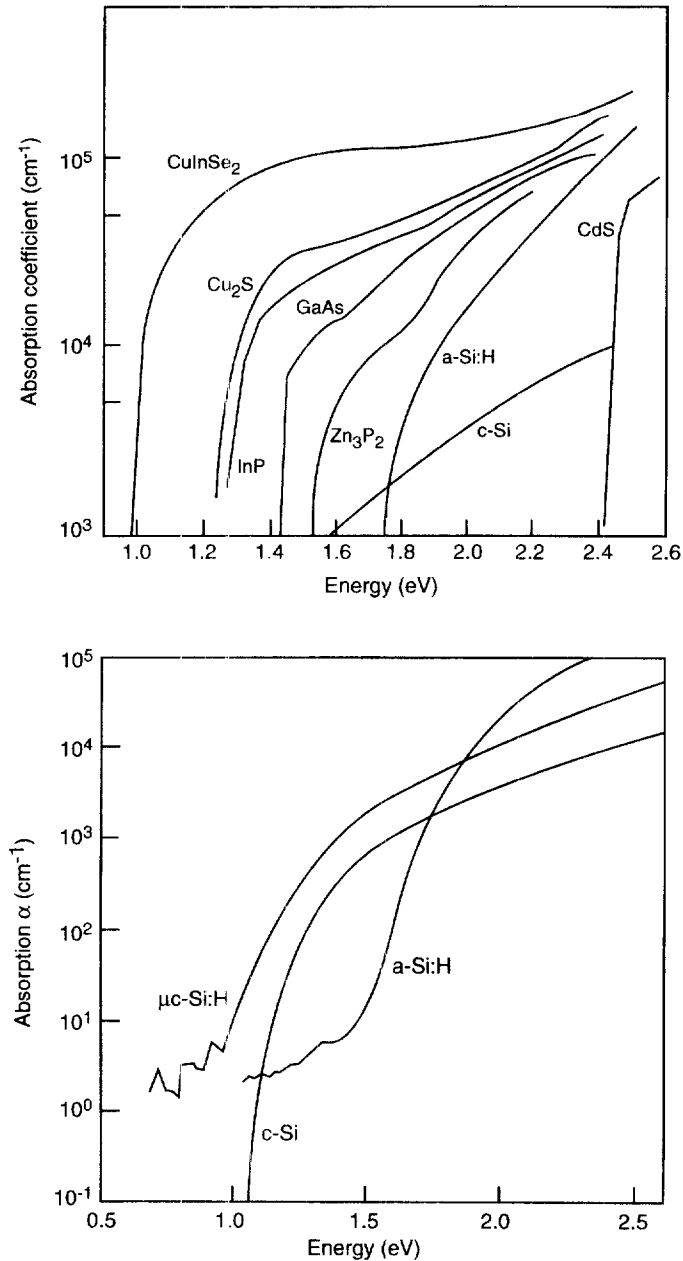


Fig. 30. Absorption characteristics, comparing various photovoltaic materials.

is usually not with the measurement, but rather with inherent change(s) in the cell itself. Recently, the U.S. industry has self-imposed a more rigorous set of measurement and reporting standards for the amorphous technologies which has led to the documentation of a “stabilized” value for the performance [406]. These conditions include the determination of the performance after exposure of the device under accepted test parameters.

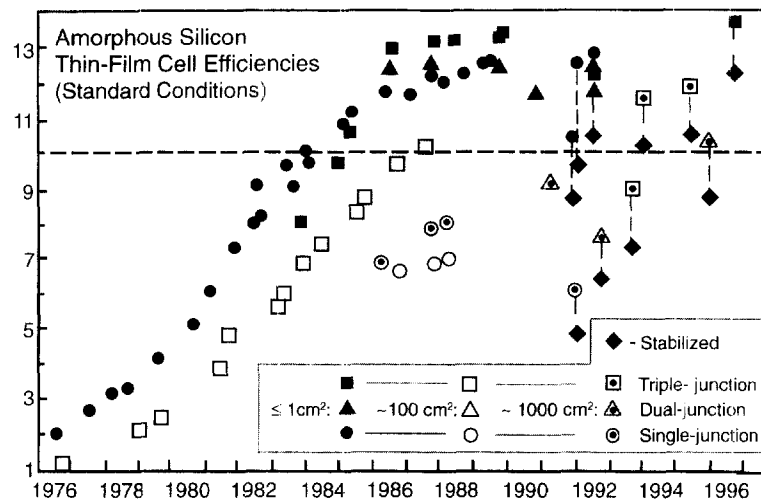


Fig. 31. Evolution of amorphous Si:H-based solar cell efficiencies as a function of time.

usually 600 h (but possibly as much as 1000 h) of light exposure under AM1.5 spectrum, 100 mW/cm<sup>2</sup> irradiance, and at 60 °C operating temperature. Most recent performance accomplishments are reported as “stabilized”, whether referring to cells or modules, and Table 8 includes these data.

The development of various device structures has been an integral part of the evolution of cell performances, including reliabilities. The various a-Si cell configurations are presented in Fig. 32, showing Schottky barrier, metal-insulator-semiconductor (MIS), single-junction (*p-i-n*), and tandem (dual- and triple-junction) designs [407]. The first cells were primarily metal/semiconductor junctions, as depicted in Fig. 32(a). Severe stability problems were inherent to the Schottky barrier design, although it continues to serve a useful purpose for research diagnostics. In 1978, a thicker intrinsic or “*i*” region was introduced leading to the *p-i-n* structure (Fig. 32(b)). The *p-i-n* cell has the advantages of reproducibility, larger area fabrication, control of cell parameters including longer carrier lifetimes, higher efficiencies, and better stability. Most current cells are based on this design. The cell configuration was further engineered with stacks of amorphous cells (called heterostructure tandem cells) as shown in Fig. 32(c), which were used to effectively increase output voltages. These cells could also use the incident light better by engineering the bandgaps through varying the composition of the various cell layers. Many of the improvements in the operating characteristics of these cell types are attributable to the increased understanding of the material and improvements in the film quality. Research efforts continue with new cell structures— including those using a-Si:C and a-Si:Ge alloys for bandgap variation, superlattice windows, random reflection interfaces, optical reflective contacts for multiple light passages, and new deposition methods.

The population of methods for producing solar-cell quality a-Si alloys has been expanding. Plasma deposition (glow discharge) remains the major film production method, and the method of choice for commercial ventures [408–410]. Its relatively low deposition rate has spurred work in reactive sputtering, chemical vapor deposition, sputter-assisted plasma CVD, and plasma deposition of higher order silanes, photo-assisted CVD, plasma confined CVD, and electron-cyclotron resonance (ECR) CVD [411–413]. Among newer approaches



Table 8. Summary of confirmed thin-film amorphous silicon-based solar-cell efficiencies and related parameters. Data are presented for various cells to give indications of improvements and scope of device development. Measurements were performed under 25°C, 1000 W/m<sup>2</sup>, ASTM E892 global conditions unless otherwise noted. The area definition used for non-concentrator cells is total area. The independently confirmed efficiencies in this table are from standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Organization	Comments
<i>Single-junction cells</i>							
1/89	3.960	874	15.62	71.3	9.7	ARCO Solar	a-Si : H (not stabilized)
1/91	0.998	872	16.54	71.2	10.3	APS	a-Si : H (not stabilized)
10/90	1.06	864	16.66	71.7	10.3	Chronar	a-Si : H (not stabilized)
2/88	0.27	940	15.2	69.4	9.9	ECD	ITO/a-Si : H/ss (not stabilized)
11/87	0.28	862	17.6	65.8	10	IEC	Photo-CVD a-Si : H (not stabilized)
9/89	0.99	886	17.46	70.4	10.9	Glasstech	a-Si : H (not stabilized)
4/92	1.00	887	19.4	74.1	12.7	Sanyo	a-Si : H (not stabilized)
4/87	1.08	879	18.8	70.1	11.5	Solarex	a-Si : H (not stabilized)
12/86	0.10	878	16.6	72.2	10.5	Spire	a-Si : H (not stabilized)
<i>Dual-junction cells</i>							
1/92	0.28	1621	11.72	65.8	12.5	USSC/Cannon	ITO/a-Si : H/a-SiGe : H/ss (not stabilized)
10/87	0.76	1685	9.03	68.1	10.3	Solarex	a-Si : H/a-SiGe : H (not stabilized)
<i>Triple junction cells</i>							
2/88	0.27	2541	6.96	70	12.4	ECD	ITO/a-Si : H/a-Si : H/a-Si/Ge/ss (not stabilized)
12/92	1.00	2289	7.9	68.5	12.4	Sharp	a-Si : H/a-Si : H/a-SiGe : H (not stabilized)
<i>Tandem with other cell types</i>							
4/88					14.6	ECD	a-Si : H/CuInSe <sub>2</sub> mechanical stack

is the hot-wire technique [414–416], which has produced a-Si : H material with superior electro-optical properties, better stability, and lower hydrogen content requirements. The variety of useful methods, as well as the introduction of multiple-chamber deposition systems [417], has made this technology among the leaders in large-area production and manufacturing. A-Si : H cells now account for about 15% of the world photovoltaic market [29].

Table 8 provides a summary of a wide number of confirmed a-Si cell parameters, covering

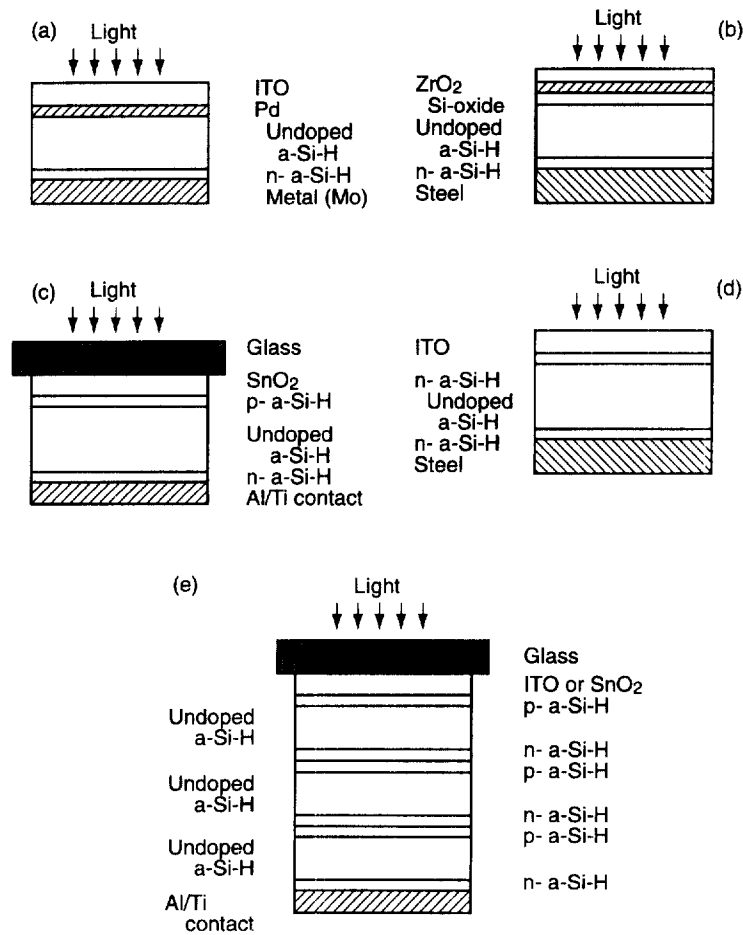


Fig. 32. Cross-sectional representations of various a-Si:H structures.

single-junction and multijunction approaches. This table cites both initial and stabilized performance characteristics, and the reader is cautioned to refer to the comments column of Table 8 to discern the cell measurement condition. One of the better single-junction ( $p-i-n$ ) cells is that produced by Sanyo, with the  $I-V$  and spectral response characteristics presented in Fig. 33 [418]. The 12.7% efficiency (1.0 cm<sup>2</sup> area) is the initial value, but represents a champion performance for the single-junction technology. Figure 34 presents the champion performance for a triple-junction (a-Si:H/a-SiGe:H/a-SiGe:H) device developed by USSC [419]. The initial  $I-V$  characteristics are shown in Fig. 34(a), with the stabilized (12.1% after 1000 h light exposure) cell in Fig. 34(c). The quantum efficiency (Fig. 34(b,d)) provides a good representation of the ability to match the total cell response to the incoming AM1.5 sunlight, with the top junctions having bandgaps adjusted by hydrogen content, and the low-bandgap cell associated with the a-Si:Ge:H alloy.

This cell is the highest efficiency stabilized cell reported at the time of this publication, and is a result of careful engineering of the device by the USSC team [420]. The top cell (matched to the blue portion of the spectrum) has an optical gap of  $\sim 1.8$  eV for the  $i$ -layer.

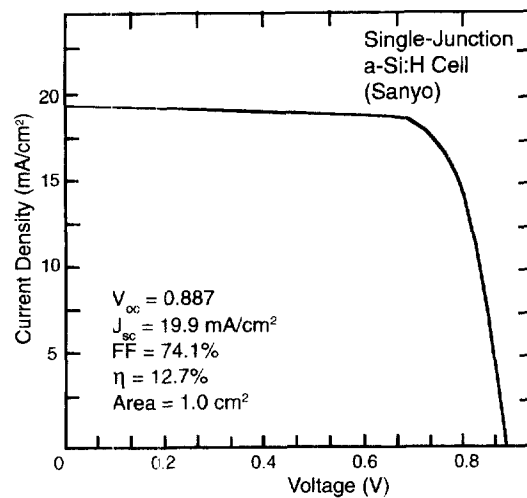


Fig. 33. 12.7 % single-junction a-Si:H solar cell: (a) light I-V characteristics; and (b) spectral response.

The *i*-layer of the middle cell has about 15% Ge, and a bandgap of  $\sim 1.6$  eV. The bottom cell is engineered in the red portion of the spectrum, with a  $\sim 1.4$  eV bandgap. The back reflector performs two functions: (1) it scatters the light at an angle higher than the critical angle for total internal reflection and (2) it must have adequate reflectivity and contacting characteristics. The ZnO in this structure is used to prevent interdiffusion of the Ag and the *n*-layer. The technical improvements in this structure claimed by USSC, shown schematically in Fig. 35, include attention to three areas to enhance the stability. First, the *i*-layers are improved with hydrogen dilution (described in the next section) of the gas mixtures. Second, the *p*-layers are microcrystalline (lower optical loss) with improved boron doping. Third, the interfaces have been engineered to provide bandgap profiling to assist in the hole transport that has inhibited effective collection mechanisms.

## 6.2. Device stability issues

For any photovoltaic technology to reach acceptance by a broad market constituency, both cells and modules must have long-term stability. Once moderately efficient a-Si:H cells were produced, the light-exposure instabilities became a concern. The *Staebler-Wronski Effect* [401, 402] is named after those who first reported it in 1977. A number of models accounting for the origin(s) of this light-induced degradation have been proposed, and several are now growing in acceptance as fundamental to the process [421–437]. Amorphous cells exhibit changes in performance after exposure to light, independent of their cell configuration, whether Schottky, MIS, or *p-i-n*. In general, most of the degradation is observed in the first 48–72 h of operation and is accompanied by a drop in efficiency of 10–50%. The major photodegradation is manifest in a change in the device fill factor [421].

The light-induced degradation problem has become one of the most investigated phenomena in photovoltaics, because of its obvious impact on this promising and expanding technology [421–423]. Almost every conceivable experimental technique has been used to explicate the effect(s), including photoluminescence, electron-spin resonance, absorption spectrophotometry, transient photoconductivity, deep-level transient spectroscopy, surface

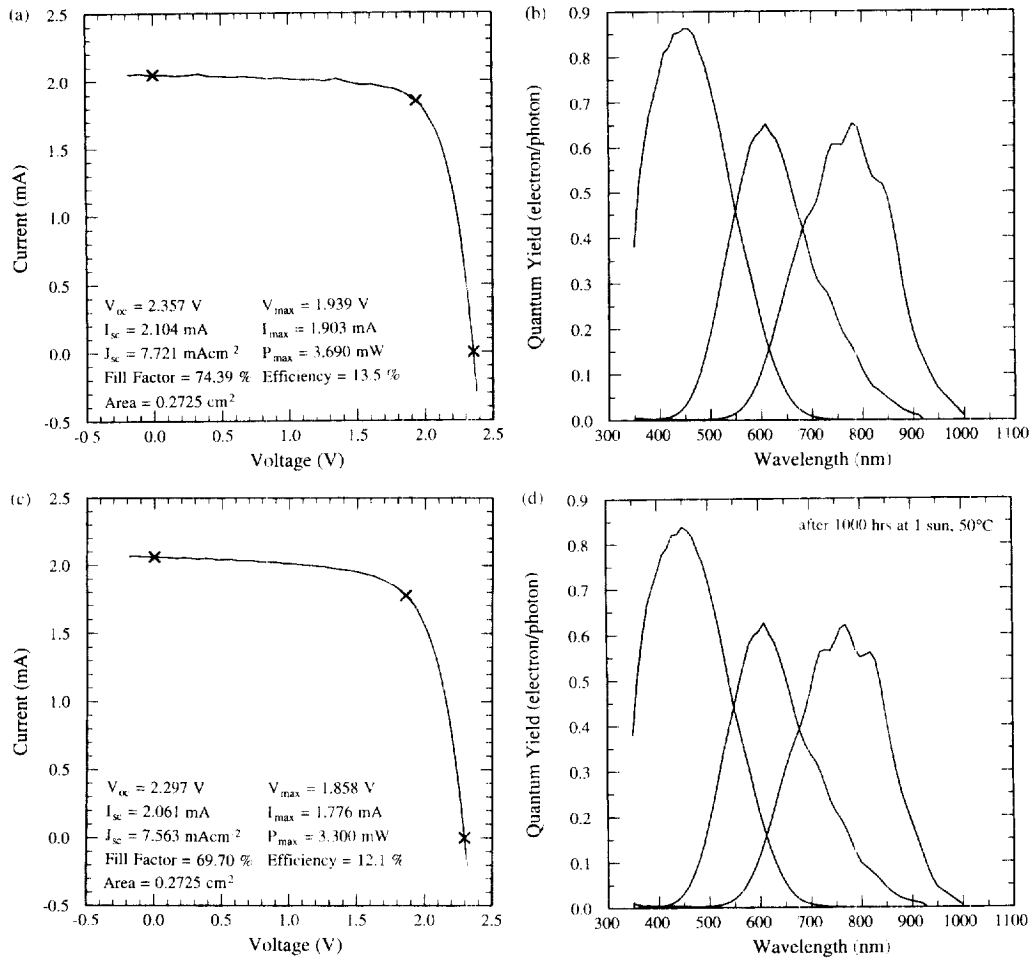


Fig. 34. Triple-junction a-SiGe:H/a-Si:H/a-Si:H thin-film solar cell: (a) initial I-V characteristics; (with (b) spectral response); (c) stabilized I-V characteristics (12.1 %); (d) spectral response of stabilized device.

analysis spectroscopies and spectrometries, Fourier-transform infrared spectroscopy, synchrotron-radiation electron spectroscopy, proximal probe (scanning tunneling, atomic force, ballistic-electron energy microscopy/spectroscopy) imaging and nanocharacterization techniques, and more conventional electro-optical methods [428]. Data have been reported on the kinetics of the annealing process, the reversibility under various external stresses, the incident-light wavelength dependence of the effect, the temperature dependence of defect creation, impurity concentration, electron-bombardment doping, film hydrogen levels, film internal stress, substrate effects, source-silane gas composition and purity, etc. The results have been reported by numerous laboratories, using many techniques, and the extensive experiments have been performed on many different a-Si:H films [429]. Intercomparisons and round-robin collaborations have added to the understanding through the concentrated

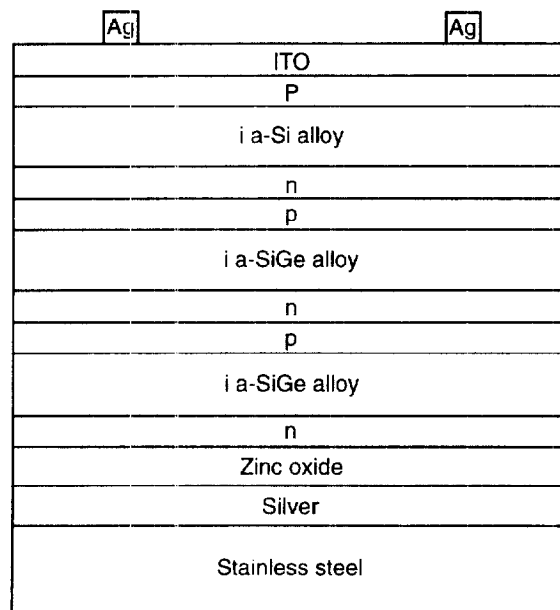


Fig. 35. Cross-sectional representation of triple-junction stabilized device.

evaluation of results. Common to most observations is that optical exposure of the semiconductor increases the density of neutral Si dangling bonds. The optical exposure produces metastable states in the bandgap that move the Fermi level towards mid-gap with increasing defect population. These metastable defects in undoped a-Si:H are produced by recombination of excess carriers, after these excess carriers are created, either by illumination or by carrier injection. The general observed properties associated with the light-induced effect in undoped a-Si:H films and a-Si:H solar cells are summarized in Table 9.

The problem remains an important and tenacious one for this technology. The reasons are *scientific* (amorphous semiconductor physics is still embryonic and developing); *experimental* (results, devices, and material still vary from laboratory to laboratory); and *political* (research and industry groups remain mildly reluctant to publish sensitive data, and funding sources/customers limit investments/purchases). However, this area has advanced significantly in its openness, and there is now some consensus in both sharing results and understanding the problems. The general major features of the light-induced degradation effects have been identified, and are compiled in Table 9. Progress has continued [421–423]. Control of material quality and doping impurity concentrations helps to minimize the degradation. Stability data on multijunction cells show that they are currently more stable than single-junction structures, primarily because the layers (especially the *i*-layers) are thinner, the current is lower, and the electric field is not confined but is spread over more of the material. Controlled doping of the intrinsic amorphous layer with either boron or phosphorous (or both) improves stability, but at the cost of a decrease in efficiency. Hydrogen dilution of the source gas during a-Si:H growth (illustrated in Fig. 37) has been effective in minimizing cell changes due to light exposure [430]. First reported in 1981, the dilution process provides the presence of excess hydrogen during deposition that passivates

Table 9. Summary of observations of light-generated changes in a-Si:H solar cells, and consensus light-induced properties and research issues for a-Si:H solar-cell technology

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*Light-induced changes in a-Si:H materials and cells*

- Rapid decrease in cell efficiency during first 48 h, followed by much less rapid change (saturation)
- Changes are associated with changes in properties of the undoped *i*-layer
- Light-induced changes are reversible by thermal annealing at 150–200°C
- Magnitude of change depends on thickness of *i*-layer: cells with thin ( $<0.3 \mu\text{m}$ ) *i*-layer easier to stabilize
- Cells operating above 90°C change less (defect creation and annealing rates are similar)
- Cells illuminated through *p*-layer of *p-i-n* cells are more stable than when illuminated through *n*-layer
- Changes in cell can be induced by either light or by current injection in dark
- Addition of B or P (p.p.m. concentrations) to undoped layer sometimes improves cell stability (but lowers efficiency)
- Light exposure increases the diode quality factor
- The  $\mu\tau$  product and hole diffusion length decreases with light exposure

*General technical observations of light-induced effects*

- Neutral silicon dangling bonds increase on exposure to light
- Density of mid-bandgap states increases on exposure to light
- Metastable state changes to stable state by thermal annealing; reverse by carrier recombination and/or carrier capture
- Fermi level moves toward mid-bandgap
- Number of metastable states is limited
- Light-induced effect is primarily a bulk (not surface) effect
- Light-induced effect is found in all high-quality, undoped a-Si:H

*Issues related to light-induced effect*

- What are the nature of the annealed and the metastable states?
  - Do metastable defects occur as dispersed or clustered in hydrogen-rich regions?
  - What is the critical population and the number of types of defect?
  - What statistics govern the annealing behaviour (defect creation)?
  - What is the role of impurities?
  - What is the role of structure?
  - What is the role and complex chemistry of the hydrogen? Is it the critical component of the process?
- 

the growing surface. The impinging species do not find a suitable site immediately and migrate along the surface before being incorporated. It is speculated that this gives rise to a better structure and associated improved material quality. This dilution method is used in a-Si:H, as well as alloys (a-SiGe:H), demonstrating its effectiveness for both silane and germane sources. (Because silane and germane have very different dissociation rates in a plasma, gas mixtures of  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  are sometimes used to deposit the alloy films.) The hot-wire technique has shown potential in improving stability, although higher cell efficiencies are still on the horizon [414–416]. The process, shown schematically in Fig. 38, uses a bright tungsten filament to decompose the source gases (silane or germane). For example, when the silane is physisorbed on the tungsten wire, it decomposes into its atomic species. Because of the wire's high temperature, these species are then re-evaporated and are subsequently deposited on the substrate.

The kinetics of light-induced degradation have been explained by three models, covering bond breaking, negative-effective correlation energy, and void defect areas. Each of these

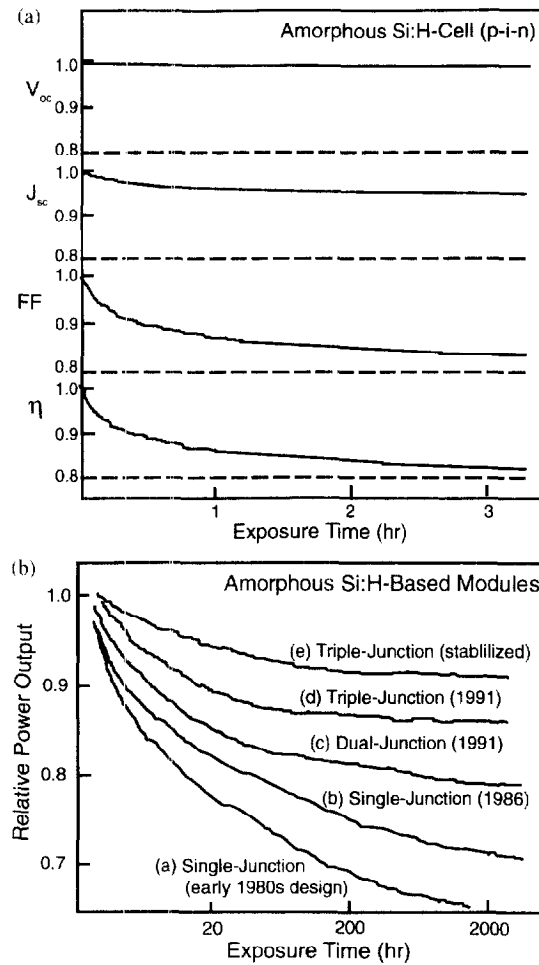


Fig. 36. Amorphous-Si:H cell parameters as function of time for ordinary cell, indicating light-generated degradation in performance.

theories has its strengths and limitations, and progress is being made. Certainly, these results, which are critical for ultimate solution of the problems, have already contributed to the engineering of the a-Si:H devices to minimize the degradation effects.

It must be emphasized that the light-exposure effects are not the only reliability issues for this technology. Experience with the extensive deployment of single-crystal Si modules has shown that problems with encapsulants, corrosion, polymer degradation, glass or polymer fracture, delamination, electrochemical effects, film and layer interdiffusions, electromigration, environmental exposures and ingresses, all exist [431–441]. In fact, initial and extensive outdoor exposure testing and laboratory measurement indicated that the amorphous and other thin-film technologies have special problems due to device structures, configurations, current densities, cell size and separation, laser and other scribe lines, metallizations, etc. Of equal importance to the *cell* stability issues are *module* reliability

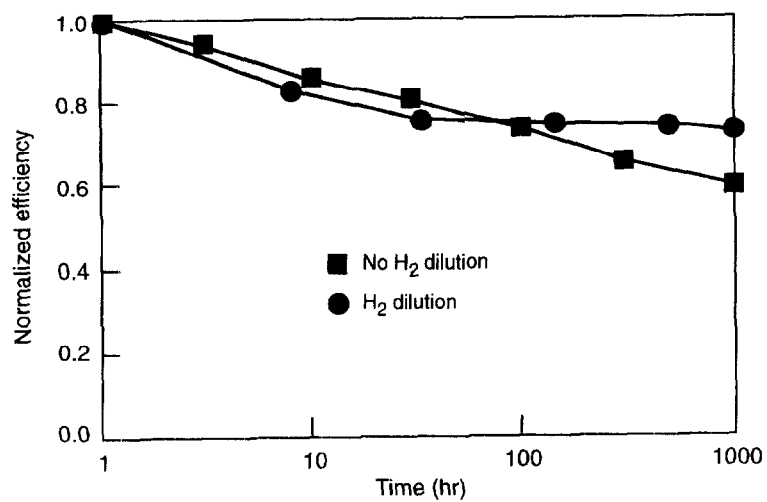


Fig. 37. Effects of hydrogen dilution showing beneficial effects on a-Si:H stability.

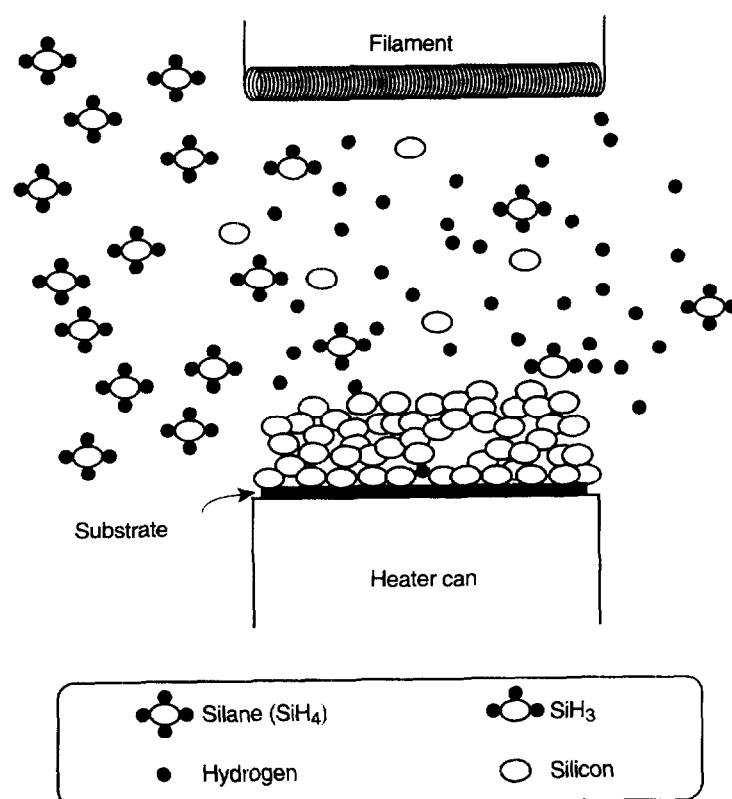


Fig. 38. Representation of hot-wire deposition process for a-Si:H solar cells. This deposition method gives indication of producing improved material for a-Si:H solar cells.



issues, and researchers and the photovoltaic industry are aware of them [442]. Currently several joint industry–research laboratory–university–utility partnerships are collaborating for determining and establishing reliable commercial products [443].

#### **ISSUES AND CONCERNS : AMORPHOUS SILICON TECHNOLOGY**

- **Stability and reliability :** Cells and modules have serious problems with light-generated and other stability mechanisms. The “stabilized” efficiencies of these research cells are about 50% less than other thin-film options (i.e. 12% versus 18%). Although cell and module engineering (e.g. multiple junctions) have minimized the Staebler–Wronski Effect, the stability issue remains a major research, manufacturing, and consumer acceptance issue. Module design has requirements beyond those for crystalline Si, and the ingress of any environmental entity has major influence because of the large surface-to-volume ratios involved. Stability of device and reliability of product is the major issue relating to the amorphous silicon technology. This may require the development of new methods of producing the films, new film structures (e.g. nanocrystalline Si or multilayers), or a new a-Si technology.
- **Research :** Certainly, the major research has to be focused on the major issue: stability—especially the Staebler–Wronski Effect. The arsenal of growth, processing, characterization, analysis, modeling, and theory techniques has to remain as the core program. The other issues (Tables 9 and 10), though they may relate, will continue to be of concern. But for this technology, it is stable performance that marks its future.
- **Cost of cell and module production :** The capital costs for cell and module production facilities are high. To date, most plant design has centered at about 10 MW—per year partially influenced by some reluctance to dedicate higher capital funds to larger capacities which might have to be abandoned if the technology does not realize a larger acceptance. This approach goes down the path of building experience to allow for flexibility.
- **Manufacturing capacity :** Current fabrication methods are vacuum-based and of relatively low-production rate. This is not an immediate problem, but one that could affect the viability in meeting longer term goals. The objective might be to increase the production speed by at least a factor of 10 to ensure competitiveness.

### **7. ON AND BEYOND THE HORIZON**

The photovoltaic research community is not sitting still, although the availability of research funding is limiting the extent of investigations into new materials, novel approaches, and other alternatives to the direct conversion of sunlight into electricity. The past 20 years have provided technologies that were not previously considered : the next 20 years should be expected to render similar results. The creativity and persistence of the scientists, engineers, and technologists will continue to be the basis for extending the opportunities and potential of photovoltaics. Some indications of the future have their beginnings in these times. This section cites some of these novel and promising PV options, most of which have emerged only in the past few years. Photovoltaics should be expected

Table 10. Summary of confirmed photovoltaic module efficiencies and related parameters. Measurements were performed under conditions defined in Table 1. Aperture area is used unless otherwise stated. The independently confirmed performance parameters in this table are from standard measurement laboratories, including NREL, FhG-ISE, Sandia, and JQA

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$I_{sc}$ (A)	FF (%)	Efficiency (%)	Organization	Comments
<i>Crystalline silicon</i>							
4/96	787.0	5.6	3.92	80.1	22.3	UNSW	PERL cells
10/94	1017.0	14.6	1.36	78.6	15.3	Sandia	HEM multicrystalline cells
9/94	3931.0	20.1	2.72	73.6	10.3	Texas Instruments	Spherical™ Si module
<i>CuInSe<sub>2</sub>-based</i>							
6/88	938.0	25.9	0.637	64.0	11.1	ARCO Solar	ZnO/(Cd,Zn)S/ CuInSe <sub>2</sub> ; 55 cells
5/91	3883.0	37.8	2.44	64.0	9.7	Siemens Solar	ZnO/(Cd,Zn)S/ CuInSe <sub>2</sub>
4/94	69.1	7.46	0.173	68.0	12.7	Siemens Solar	ZnO/(Cd,Zn)S/ Cu(In,Ga)Se <sub>2</sub>
7/94	3859.0	27.2	2.40	61.0	10.3	Siemens Solar	ZnO/(Cd,Zn)S/ Cu(In,Ga)Se <sub>2</sub>
10/94	202.0	11.5	0.637	64.0	9.0	EPV	ZnO/(Cd,Zn)S/ CuInSe <sub>2</sub>
5/93	846.0	29.7	0.284	57.0	5.7	ISET	ZnO/(Cd,Zn)S/ CuInSe <sub>2</sub>
12/86	97.0	1.78	0.774	64.0	9.1	Boeing	ZnO/(Cd,Zn)S/ CuInSe <sub>2</sub>
4/96	90.0	9.33	0.181	73.7	13.9	Univ. Stuttgart	Submodule, 15 cells
<i>CdTe</i>							
4/96	6728.0	95.0	0.9666	66.8	9.1	Solar Cells, Inc.	Submodule, 12 cells Outdoors, 1032 W/m <sup>2</sup> total irradiance, 24°C module temperature
2/95	83.4	9.406	0.1435	64.9	10.5	ANTEC	
2/95	6693.0	92.8	0.966	66.0	8.6	Solar Cells, Inc.	
5/93	63.60	6.62	0.137	69.0	9.8	Solar Cells, Inc.	Outdoors, 1013 W/m <sup>2</sup> total irradiance, 31°C module temperature
8/93	3528.0	44.2	1.1	57.0	7.7	Golden Photon	
9/91	832.0	21.0	0.573	55.0	8.1	Photon Energy	Outdoors, 1013 W/m <sup>2</sup> total irradiance, 33°C module temperature
10/88	100.0	9.63	0.125	57.0	6.8	AMETEK	
<i>Amorphous Si:H</i>							
12/92	100.0	12.5	0.13	73.5	12	Sanyo	a-Si:H (not stabilized) submodule
1/94	11634				4.4	APS	a-Si:H (stabilized) production module
9/93	1200.0				8.9	Fuji	a-Si:H/a-Si:H (stabilized)

Table 10. Continued

Date	Area (cm <sup>2</sup> )	$V_{oc}$ (mV)	$I_{sc}$ (A)	FF (%)	Efficiency (%)	Organization	Comments
12/93	906.0	2.40	6.57	67.5	11.8	USSC	a-Si : H/a-Si : H/a-SiGe : H (not stabilized)
12/93	903.0	2.32	6.47	61.2	10.2	USSC	a-Si : H/a-Si : H/a-SiGe : H (stabilized)
11/95					12.1	USSC	a-Si : H/a-Si : H/a-SiGe : H (stabilized); initial efficiency = 13.4%
<i>Cross-technology</i> 6/88	853.0			64.0	13.7		a-Si : H/CuInSe <sub>2</sub> mechanical stack; total area efficiency = 12.9%
<i>Concentrator</i> 3/93	41.40				25.1	Boeing	GaAs/GaSb, 3-mechanical stack, 57 suns
4/89	1875.0				20.3	Sandia/UNSW/ENTECH	Crystalline Si, 20 cells, 80 suns

to reflect advances in other scientific areas; the playing field is broad and the expectations should remain high.

### 7.1. Thermophotovoltaics

The first of the “emerging” PV-related areas is not a new technology. It has its most active research and development origins in the late 1970s [444–446]. However, it serves as an example of the rebirth of an area that was theoretical feasible, but much before its technological time. It should also serve as a signal for funding sources to be alert to the reintroduction of early concepts that can be viable because of advances in related science and engineering.

Alloys of InP with GaAs (i.e. GaInAsP) have provided some promise for this photovoltaic area—thermophotovoltaics (TPV)—including some terrestrial promise and value [447]. This technology is not concerned with sunlight, but rather with radiation in the infrared region. A schematic representation of the TPV process is illustrated in Fig. 39, and includes primitively the source, emitter/reflector, and cell. The conventional approach has combined a high-efficiency photovoltaic cell with a selective radiator having its emission band near the bandedge of the cell. The early incursions into TPV involved semiconductors with bandgaps in the 0.9–1.1 eV range (primarily Ge and Si), that matched to spectra having temperature equivalents above 2000 K. These temperatures made it very difficult to engineer real systems. The ability to produce lower bandgap semiconductor devices, a direct result of photovoltaic R&D, brought into reality semiconductor devices in the 0.5 eV range—

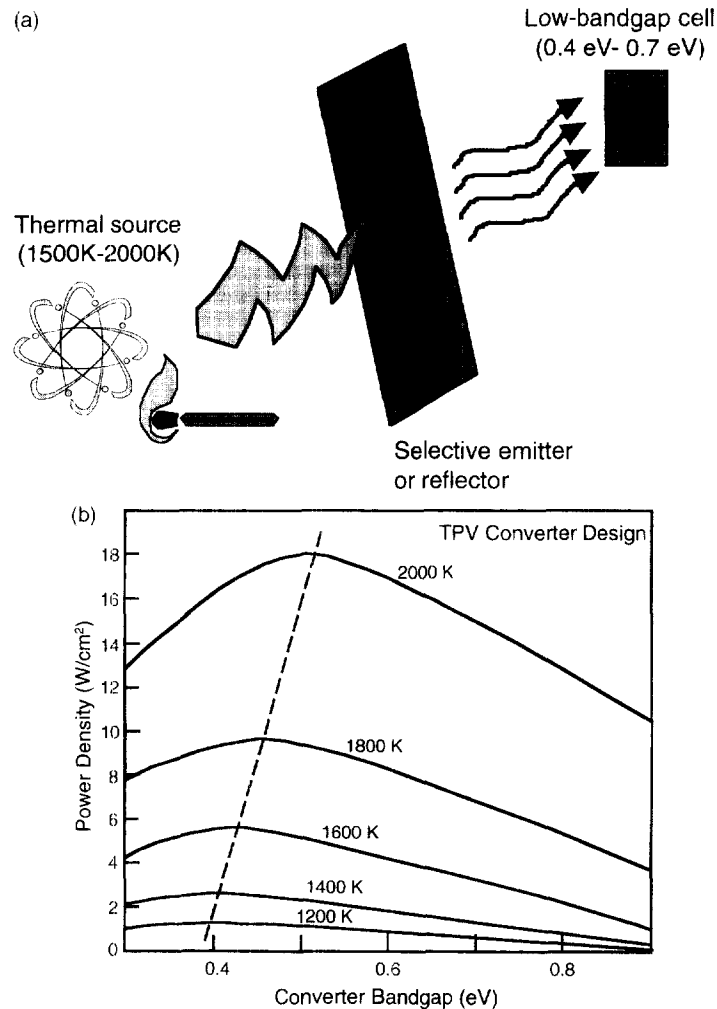


Fig. 39. Schematic representation of the TPV conversion and application process.

corresponding to temperatures of approximately 1500 K, more suitable for system realization.

Complete thermophotovoltaic systems include: (1) a fuel and a burner, (2) a radiator, (3) a long-wave phonon recovery mechanism, (4) a PV cell (converter), and (5) a waste-heat recuperation system. Currently, radiant burners operated in the 1500 K region are near-ideal for TPV applications [448, 449]. These are primarily porous ceramics (SiC) and metal-mesh designs. For terrestrial applications, operation of burners above 1500 K poses problems since  $\text{NO}_x$  emissions increase exponentially with temperature. One interesting approach is that proposed by Broman and Marks, using the flame produced by efficiently burning wood powder to provide the irradiance [450]. This renewable source has laboratory demonstration, and further development is underway to determine economic and technical viability. Emitters are of two major types. (1) Selective, primarily rare-earth oxides, in which the valence electrons are screened and the rare-earth ions behave like gaseous ions

and emit line rather than continuous radiative spectra. Examples are:  $\text{Yb}_2\text{O}_3$  for Si;  $\text{Er}_2\text{O}_3$  for Ge or GaSb, and  $\text{Ho}_2\text{O}_3$  for the III–V alloys [451–453]. Recently, Er- and Yb-doped yttrium aluminum garnet (YAG) emitters have received attention [454]. Their temperatures are  $\sim 1423$  K, although these emitters have not been optimized. (2) Broadband emitters which are black- and gray-body types that emit over a wide range of wavelengths. The optimum range corresponds to 1300–1700 K, and include several based on SiC. This includes the spine disc burner/emitter developed by Fraas *et al.* [455]. The broadband emitter approach is simpler than the selective emitter, easier and less labor intensive to manufacture, more durable, and less costly. The PV converters or TPV cells are the central part of the system. A number of semiconductors, notably InGaAs (0.5 eV) and InSb (0.47 eV), have shown exceptional promise, and commercial products have been introduced [446]. Thin-film Ge is also proposed as an economic alternative, although this semiconductor presented several technical problems in trying to produce effective single-crystal devices for this application [457]. In any event, TPV is a technology that deserves monitoring, since the current interest and advances in cell and system performance have brought some increased speculation and funding into this area. The recuperation recovers the sub-bandgap photons, and returns them to the radiation surface for reabsorption. This is accomplished by optical control using plasma-interference filters, back-surface reflectors, and resonant filter arrays [458].

TPV is a current and intensive research area. The bottom line is the system efficiency, and the R&D interest is in all TPV components. Determination of the TPV device efficiency is problematic since it depends upon the system (emitter type) in which it is used, although some methods involving gray- and black-body emitters have been investigated [459]. Current limitations to commercialization for terrestrial product hinges mainly on the cost of the converters, which use expensive III–V substrates. [Editors Note: *Renewable and Sustainable Energy Reviews* will publish an extensive review of thermophotovoltaics in a coming issue.]

### 7.2. Nanocrystalline electrochemical devices: the Grätzel cell

This technology is also one that received attention in the 1970s and 1980s [460], but has been refined to enhance power generation capability and stability. The junction between an illuminated semiconductor and electrolyte generates a photovoltage, similar to a conventional solar cell. This cell approach has been restricted because of materials stability problems. The introduction of oxide semiconductors to this technology reduced the potential of photo-oxidation (photocorrosion), particularly for *n*-type semiconductors in which the photogenerated minority carriers at the interfaces act as oxidants. However, oxide semiconductors, such as  $\text{TiO}_2$ , have bandgaps in the 3 eV range—insensitive to the solar spectrum. The extension of the photoresponse across the visible portion of the spectrum has been achieved by separation of the two steps of the photovoltaic process. The oxide semiconductor in the electrochemical system is sensitized by a monolayer of an electroactive dye having an optical absorption band extending across the width of the visible spectrum. Charge separation occurs by electron loss from the photoexcited dye to the semiconductor substrate. The cell, sometimes termed the *Grätzel cell* after its discoverer and principal proponent, is illustrated in Fig. 40 [461, 462]. Following absorption of a photon, the excited state of the dye is such that relaxation by electron loss to the semiconductor substrate is possible, leaving the dye molecule as an oxidized species. The original ground state of the dye is restored by a charge transfer reaction with the redox electrolyte. The cell is completed

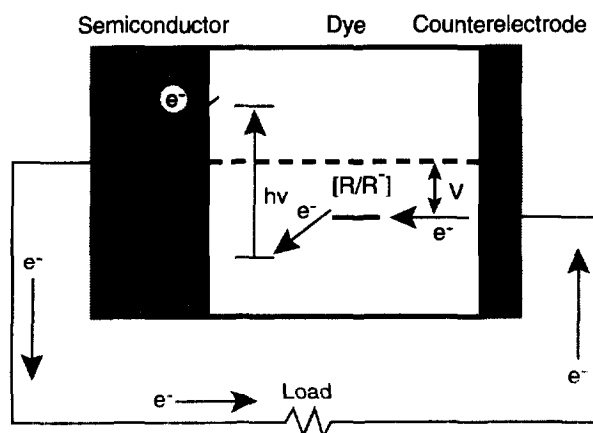
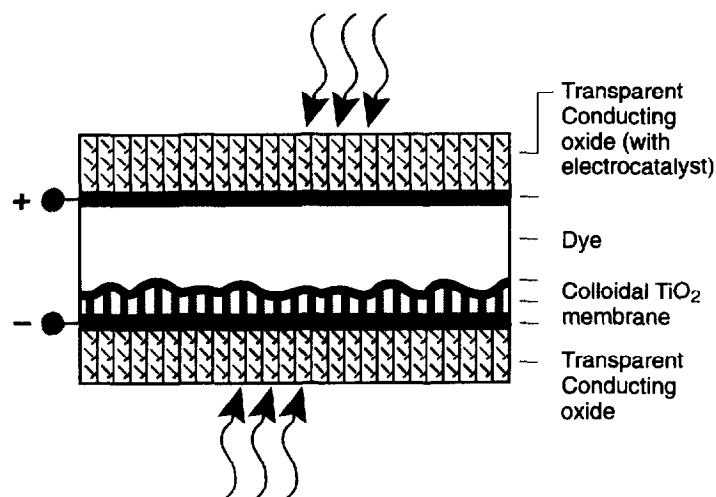


Fig. 40. Grätzel (electrochemical) cell: (a) cross-sectional representation, and (b) process involved in photoconversion.

by a metallized counterelectrode at which a reduction reaction with a redox system takes place.

Early experiments in sensitization photoelectrochemistry did establish the feasibility of the spectral extension of the photoresponse of the device to the photon energy lower than the bandgap of the substrate semiconductor, although the performance efficiency was low relative to solid-state counterparts. The fabrication of a practical device recognized that the physics of the charge separation and transport did not require a regular extended crystal structure with perfect or planar surfaces. Porous and polycrystalline surfaces provide comparable performance levels for the dye-sensitized device. No minority-carrier recombination problems concern this cell because these carriers are not present in the semiconductor. After injection, the electrons (within the semiconductor lattice) are separated

spatially by a potential barrier from the oxide-semiconductor dye. The reverse process of electron loss from the substrate to the oxidized surface species is limited due to the chemistry. The electrical connectivity necessary for the transport of the injected charge from the interfaced led to the engineering of the morphology of the oxide semiconductor. Screen printing inks of  $\text{TiO}_2$  followed by air sintering have been typically used to provide the best layers—layers that are textured and nanocrystalline in structure. Some enhancement of short-circuit currents is also gained by processing of the grains leading to their encapsulation.

Dye development has been (and remains) an active area of interest and activity. Ruthenium has been a common sensitizer [463]. Charge exchange between the dye and the redox system supported by the electrolyte is extremely rapid. Suitable iodine/iodide redox couples have been achieved with aqueous, organic, and molten-salt electrolytes. Electrolyte optimization is still an area of concern.

Grätzel cells with near-10% efficiency have been reported [464]. The accurate measurement of these devices is more complicated than for conventional photovoltaic cells because of the time constants involved with the absorption and recombination processes [465]. Inaccurate evaluations of performance have been reported because of lack of consideration of these effects, especially during the spectral response measurement. A champion  $I$ - $V$  characteristic for a Grätzel cell is presented in Fig. 41. Many of the cells have been reported to have better performances at lower irradiance levels.

The technology is promising because it involves a predicted low-cost processing for large areas. However, the technology is not without its critics. Stability remains a question, although many refinements and improvements have led to demonstrations of enhanced performance in this area. Because of the relative infancy of the technology and less-widespread work on development, little is known about the factors that may limit the lifetime of devices (cells and modules) in extended operating conditions. The industry has been slow to invest in this technology area—perhaps because it competes directly with other, more mature thin-film options.

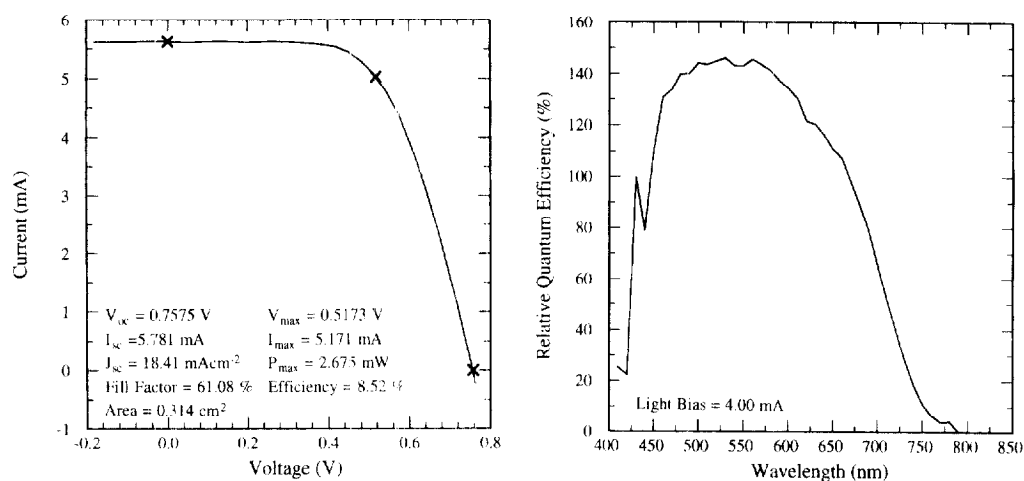


Fig. 41.  $I$ - $V$  characteristics and spectral response for electrochemical Grätzel cell.





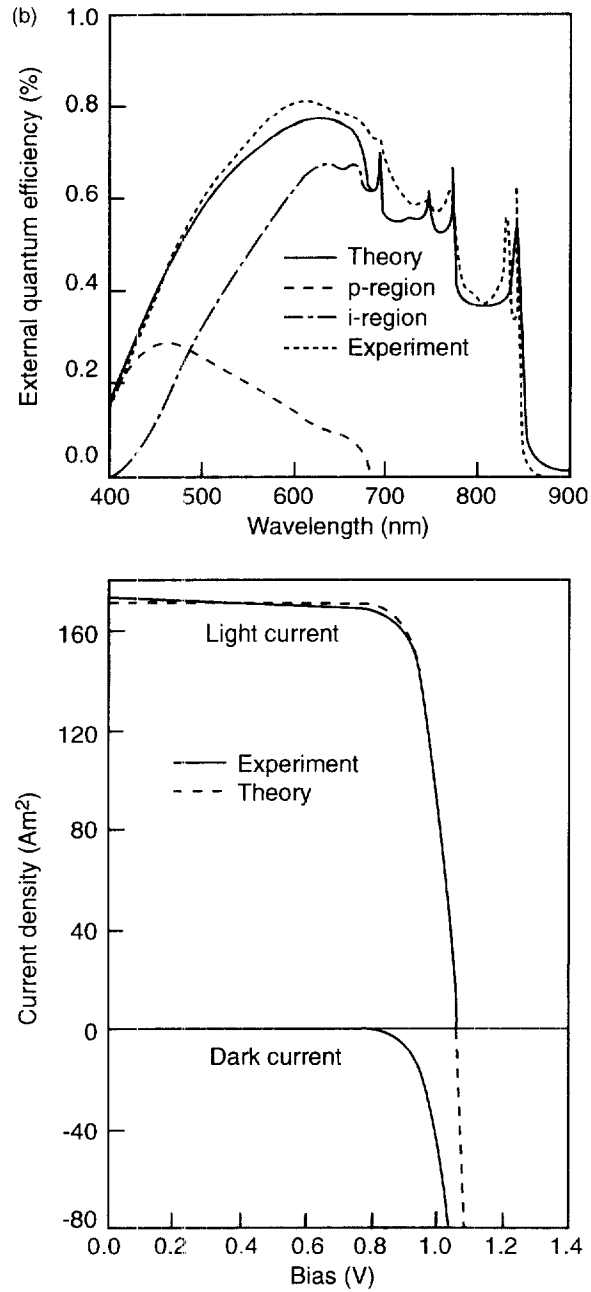


Fig. 42(b).

device, because of poor minority-carrier lifetimes and higher-than-optimum bandgap. More recent work has been with GaAs or InP/strained InGaAs wells. Ragay *et al.* have incorporated MQW in the *i*-region of *p-i-n* cells, and analyzed the performance of GaAs/InGaAs *p-i-n* MQW solar cells with fifteen 80 Å  $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  quantum wells incorporated in the *i*-

region of the  $p-i-n$  GaAs cells [468]. The major conclusions related to the effects of the thickness of the GaAs barrier on the cell parameters, but did purport to demonstrate the operation of the MQW approach.

Some problems exist with the MQW structure, which must operate at a small forward bias for a solar cell. This operation point is difficult to realize for the MQW. (In comparison, quantum-well lasers operate in high-forward bias conditions, and modulators and photodiodes operate in negative bias.) Another problem is cost. It is proposed that to make the MQW solar cell cost competitive, concentrator applications are a necessity. In fact, because carrier escape from the wells is primarily thermally activated, MQW cells have some advantage at higher temperature operations than conventional cells. This cell is currently of research interest, but controversy surrounds its predictive operation as a solar cell. Theoretical analyses of the carrier transport and device physics provide some doubts about any extensive gain in performance over a conventional III-V cell. Araújo *et al.* reviewed detailed balance theory for the MQW cell and concluded that the same assumptions hold for MQW solar cells and exempt that device from exceeding efficiencies for the single-junction device [469]. They supported their analysis with some experimental measurements. Because of the complexity of the structure and related complicated manufacturing/processing and the cost of the materials required, unless large gains in performance are attained, the device would not meet cost requirements for terrestrial applications. In any case, consideration of this novel device has contributed to the knowledge base of III-V cell operation and has provided new avenues of research at the leading edge of science.

#### 7.4. Porous silicon

Porous silicon first received attention because of visible light emission and bandgap widening [470, 471]. This material is usually formed on crystalline Si substrates at room temperature by anodic dissolution processes in HF-based electrolytes [472]. Light-emitting porous Si has a porosity in the 30–90% range. The material exhibits photoluminescence and electroluminescence, qualities that give indication that the material would be suitable for photovoltaic application [473]. Advantages of using porous Si include: (1) the bandgap can be varied over some range around 1.5 eV. The apparently wider bandgap of the porous Si provides its use as a window in a heterojunction cell, the absorber of the top cell of a tandem configuration, or for establishing a back- or front-surface field in a diffused-junction Si cell; (2) the highly textured surface provides for enhanced light trapping and potential as an antireflection coating [474]; (3) the porous Si formed on the back of a wafer (e.g. cast or Czochralski) can be used as an external gettering agent for impurities; (4) the photoluminescence property provides the advantage of converting UV and blue light into longer wavelengths that are more suitable for conversion in a Si cell; and (5) it can be produced in large areas and incorporated into solar-cell manufacturing lines.

In contrast to these advantages, there are some problems. The porous Si has high resistivity and little is understood about the photogeneration of carriers and charge carrier transport mechanisms. It is also difficult to dope the material with the conventional processes used in Si cell fabrication. It is especially sensitive to any high-temperature treatments.

Photodetectors and primitive solar cells have been demonstrated. However, few higher efficiency devices based on porous Si have been reported. The use of porous Si as an optimized emitter has been shown by Bastide *et al.* to be possible in a Si solar cell [463]. The porous Si is formed in the outer region of the emitter by electrochemical etching of the surface. The emitter consists of a top layer of porous Si and a bottom layer of bulk  $n^+$  Si.

Quantum-efficiency measurements show the effectiveness of the porous Si in this configuration. The cell showed reasonable photovoltaic behavior, although the series resistance limits the fill factor—limiting the conversion efficiency. Vernon *et al.* have developed processing techniques for the porous Si cell, but have been limited by low  $V_{oc}$  [476]. The most encouraging result is that reported by Schirone *et al.*, who produced large-area solar cells by converting the Si surface into porous Si by etching in controlled solutions [477]. They reported a 100 cm<sup>2</sup> cell with an efficiency of 10.4% (AM1.5), with improved photon absorption to near infrared radiation and surface passivation.

### 7.5. Organic solar cells

Photoconductivity, photovoltage, and photovoltaic effects in organic materials have been known for a long time, and have been used in photography and xerography. The first organic solar cells were reported in the 1960s, but the investigations were overshadowed by the developments of conventional devices [478–480]. The technical environment surrounding organic solar cells is uncertain. Many R&D programs on organic solar cells have been undertaken over the past 20 years, but none have been longlived. All organic solar cells that have been tested under sunlight conditions are characterized by low efficiencies with reported efficiencies in the 10<sup>-8</sup>% to the 1% range [481]. The major drawbacks to these devices have been fill factors and poor short-circuit densities. The major benefits to organic semiconductors are potential for very low cost, *in situ* chemical production, and energy storage capabilities.

The most promising of the organic devices have been *p-n* cells with a planar perylene derivative as the *n*-type layer and a phthalocyanine as the *p*-semiconductor [481]. Efficiencies of up to 1%, with relatively good fill factors (up to 0.65), have been reported. Polymeric semiconductors such as polyacetylene *p-n* structures have realized efficiencies in the 10<sup>-3</sup>% regime [483]. These approaches do, however, provide easy fabrication and processing. Major interest in polyacetylene was due to the reports of successful *n*- and *p*-type doping and control of these layers [484].

Metal–semiconductor (MS) and metal–insulator–semiconductor (MIS) cells are more problematic. This is due to the small absorption of organic material and the barrier contacts which have small transparency. Merocyanine-based MS or MIS cells attracted some attention in the late 1970s, because of efficiencies in the near-1% region for cells [485]. Reproducibility proved to be a problem, and this is consistent with the fact that merocyanines are known for instability under sunlight.

The major problems associated with organic materials are: (1) broad photon energy absorption: many organic semiconductors have no absorption edge, but are characterized by absorption bands; (2) mobile carriers: organic semiconductors usually have narrow energy bands with low carrier mobilities due to minimal overlap of molecular orbitals; (3) doping: this is highly influenced by the processing and operation ambient; (4) contacts: ohmic contacts are difficult to obtain with organic semiconductors; (5) stability; (6) materials: this is viewed as a benefit and a problem: the number of organic semiconductors is extensive and not well-investigated for photovoltaic applications; purity and preparation are also areas of concern, especially for large-area devices; and, (6) quantum efficiency: low over the visible range of sunlight for all organic semiconductors having photovoltaic promise.

There is no extensive interest in organic solar cells currently. Investigations are rekindled from time to time. For example, when nuclear war was of intense interest, organic sem-

iconductors in general became very interesting for electronic applications due to their radiation resistance. Organic semiconductors appear to be considerations only in the far future of terrestrial photovoltaics. However, they remain a research consideration which may become feasible if materials development overcomes the problems cited above. Ruling out organic solar cells as longer term candidates would be short-sighted just because they cannot compete with current conventional approaches. Knowledge of these materials and devices is sub-embryonic.

#### 7.6. *Local defect-layer solar cells*

In 1992, a special Si solar cell with an efficiency more than 40% higher than any other Si efficiency previously attained, was reported for a  $0.07 \text{ cm}^2$  device [486]. The device, termed a junction near-local defect layer (JNLD) cell, was proposed to have enhanced performance due to the introduction of a near-junction defect layer that was very effective in light absorption and carrier-pair generation. The layer, produced by hydrogen implantation and annealing, creates defect levels within the Si bandgap and acted as a sub-bandgap photon absorber. The concept was not new, having previously been proposed and analyzed by Güttler and Queisser [487]. However, the result presented by the JNLD was surprising, and led to a series of analyses and studies to determine its validity [474a].

The major conclusion seems to be that no significant positive effect on the short-circuit current densities of the cells results from the defect layer, although this effect may depend critically on the relative position of the defect layer and the junction [488]. The defect layer has been observed to adversely affect the dark current characteristics. It is presumed that the extraordinary performance reported was due in large part to measurement error and measurement under non-standard conditions.  $V_{oc}$  lowering has been reported for devices having such defect layers, and this parameter would not depend upon layer positioning. The results have not been totally reproduced, although some partial benefits of the local defect layer have been observed. P. Wawer *et al.* fabricated cells using a  $\text{He}^+$  ion-produced LDL to analyze the effects of the defect layer [489]. Cells with these LDL have shown enhanced photogeneration, without adversely affecting the recombination performance. However, these results do not indicate that efficiencies beyond normal limits can be achieved in the Si cells [490].

#### 7.7. *Spheral<sup>TM</sup> solar cells*

This innovative approach should occupy space in a review of the current crystalline solar-cell technologies. However, due to a change in technological emphasis by the industrial developers and redirection of concurrent funding by investors, the technology is currently "on hold" while a new development group takes responsibility. This technology uses cells fabricated on Si spheres and was announced by Texas Instruments (TI) in 1990 [491, 492]. It is trademarked the Spheral<sup>TM</sup> Solar Cell, and is an outgrowth of a 1980s program on photoelectrochemical cells at TI [493].

The spheres are formed by melting millimeter-sized particles of electronic-grade material. The particles tend to take round shapes during melting due to the dominance of surface tension over other forces. As the Si solidifies, single-crystal spheres are formed, and the impurities tend to accumulate near the surface of the sphere. Mechanical grinding then removes this portion of the impurities. This melting step is repeated several times to bring the spheres to the desired purity. Solid-state treatments, such as oxygen precipitation and phosphorus gettering, are used to passivate the remaining impurities within the sphere. The

~0.75-mm diameter spheres then undergo a P-diffusion to create the junction. The cell spheres are processed into an embossed Al foil in a hexagonal pattern to provide a flexible matrix to hold them in place, to contact the spheres electrically, to mask the back side for etching, and to provide a back reflector for the light. Cells with an average efficiency above 10% have been fabricated, with yield of 90% for 10 cm<sup>2</sup> areas of the flexible foil. Prototype module efficiencies in the 8–9% range have been achieved [492, 494]. The foils themselves showed exceptional durability to mechanical stresses.

This is a situation in which the investment and economics were ill-timed for a new technology direction. Although the Spherical<sup>TM</sup> Solar Cell attracted considerable attention from the PV community, reached notable and confirmed performance levels, and predicted costs in line with most economic goals for a viable PV technology, the investment strategy did not conform to technology portfolios. Several groups had made inquiries, although a recent spherical<sup>TM</sup> restart has been abandoned.

### 7.8. Other considerations and approaches

Solar cell designs and concepts have been developing in reaction to electronic device advancements.

*Other materials.* A study and compendium of potential new materials has been provided by Ditttrich *et al.*, using a systematic mineralogy approach to the identification of candidate materials [495, 496]. This approach has screened hundreds of naturally occurring minerals with respect to their PV properties. It should be noted that a host of other materials are under consideration, such as FeS<sub>2</sub> [497], WS<sub>2</sub> [498], WSe<sub>2</sub> and MoSe<sub>2</sub> [499], and SiGe alloys [500]. The “other materials” provide a lengthy list, and the reader is referred to the recent proceedings publications from the three major photovoltaics conferences.

*Fullerenes.* Considerations for Buckminsterfullerenes, C<sub>60</sub>, for photovoltaic use have been proposed. Results of experiments include the fabrication of Schottky barrier devices (Ag/C<sub>60</sub>), investigations of bandgap and morphology of C<sub>60</sub> thin films, and the fabrication of a C<sub>60</sub>/Si heterojunction solar cell [501]. Results are preliminary, but provide an interesting application for a material in search of one.

*Holographic solar concentrators.* A holographic concentrator has the ability to act as a concentrating transmission–reflection filter [502–504]. One concept holographic concentrator device (Fig. 43), uses a single-element hologram to spectrally separate light and focus it perpendicular to the hologram in a thin, concentrated line [505]. Two or more different cells can be placed along this line such that each cell absorbs the wavelengths that are matched to their bandgaps. Because the hologram is a single element performing two functions, reflective losses are decreased. Because the hologram focuses the light into a line, long and narrow solar cells are required. This decreases shading and resistance losses from the contacts. The design also reduces the free electron path, and the related recombination rate is lowered.

A major advantage is that cooling requirements are reduced over other concentrator designs. Spectral separation prevents overheating by diffracting unwanted infrared radiation away from the cells, while the spectrally dispersed side focus replaces the common cascade. System efficiencies in excess of 40% are predicted for GaAs/InGaAs tandems. Experimental verification of the effect has been achieved, although the development of this technology is still in its infancy. Cost predictions are still uncertain, although preliminary analysis predicts achievement of ~\$0.06/kWh if technical objectives can be reached.

*High-efficiency thin films.* Most 20–30%-efficiency concepts center around single-crystal

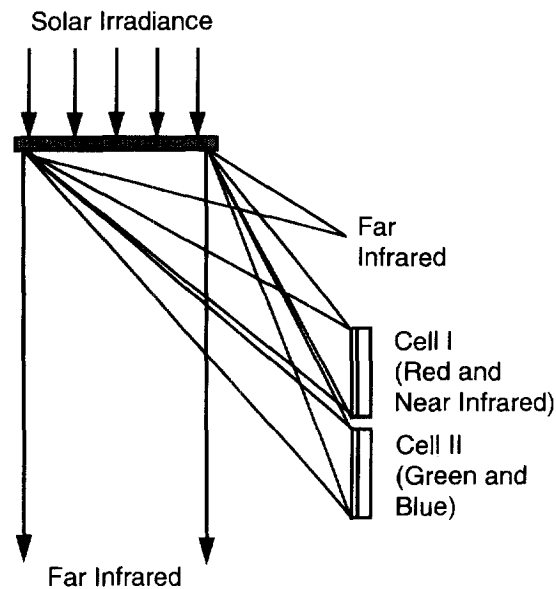


Fig. 43. Holographic concentrator device, using a single-element hologram to spectrally separate light and focus it perpendicular to the hologram.

structures. Some thin films deposited on foreign substrates, such as glass, graphite, or polycrystalline semiconductors, are also being investigated for eventual high-efficiency devices. The objective is to develop a large-area, single-crystal films (or very large-grain polycrystalline films) on these substrate [506, 507]. Candidate materials include both III-Vs (mainly GaAs) and  $\text{CuInSe}_2$ . Certainly, a good amount of work on thin-film GaAs and InP was reported in the late 1970s and early 1980s (see Appendix I), with devices in the 8–10% efficiency range. Devices were limited because of limited availability and understanding of the growth mechanisms, especially on non-structured substrates. It is conceivable that more perfect material will be able to be deposited on substrates such as glass, and this will lead to cells in the desired high efficiency range. Some indication of this potential is the 18.2% GaAs cell grown on polycrystalline Ge by Venkatasubramanian *et al.* [507]. There is also some considerable interest in  $\text{CuInSe}_2$ -based cells for space and concentrator applications [508–510]. There have been several demonstrations of the Cu-ternary devices with increased efficiencies under concentrated-light conditions, with one reported improvement in efficiency from 15.1% (1 sun, AM1.5) to 17.2% (22 suns) by Tuttle *et al.* [509]. Additionally, these thin films have shown some promise for extraterrestrial use because of radiation-resistance properties. Current work is centered on the development of high-efficiency devices on thin-glass substrates.

*Micromorph solar cells.* Hydrogenated microcrystalline silicon ( $\mu\text{c-Si:H}$ ) has been introduced as the absorber film for a-Si:H solar cells, providing better stability, more suitable bandgap characteristics (near 1 eV), and enhanced absorption (infrared sensitivity; see Fig. 30). The term ‘micromorph’ has been adapted for this cell because it combines microcrystalline and amorphous cells into a first a matrix material and then a tandem configuration for potentially superior performance [510]. The  $\mu\text{c-Si:H}$  is prepared by low-temperature (170°C–220°C) plasma deposition using hydrogen-diluted ( $\sim 3\%$ ) silane, and

the films can be grown adequately only any substrate (including glass). The grains are typically less than 100 nm, embedded in an amorphous Si:H matrix. The properties of the absorber films are controlled by grain size, topography, and the volume ratios of the crystalline to amorphous material.

Several device concepts have been realized, and completely  $\mu\text{c-Si:H}$  cell have been proposed. Tandem cells (1.72-eV a-Si:H on 1.0-eV  $\mu\text{c-Si:H}$ ) have been fabricated with efficiencies exceeding 10%. Triple-junction devices (a-Si:H/a-Si:H/ $\mu\text{c-Si:H}$ ) have also been reported with efficiencies near 10%. The positive initial indications include stability; the tandem micromorph designs are not affected by light soaking. The cells are limited by the low  $V_{oc}$  (400 mV) of the bottom  $\mu\text{c-Si:H}$  cell. It is proposed that recrystallization or improvement of the p-i interface (e.g. by controlled hydrogen dilution) can help improve this low voltage. The higher order tandems (i.e. three and four stacks) are also limited by insufficient absorption in the a-Si:H. The use of a-SiGe:H or other alloys in the middle junctions might overcome this problem. Currently, the deposition rates for the  $\mu\text{c-Si:H}$  are low (1–2 Å/s compared to the required 5–20 Å/s for large-scale manufacturing). Currently, increases in the growth rates leads to deterioration in the quality of the  $\mu\text{c-Si:H}$  material. The micromorph cells concept is in its infancy, but already has caused genuine interest and application in the thin-film solar cell industry R&D environment.

## 8. MODULE TECHNOLOGIES

The configuration of cells, electrically connected into series and parallel strings to deliver a desired voltage and current and encapsulated into a supporting structure for environmental protection and strength, is the elemental module configuration [511]. The materials used for support and encapsulation depend upon the cell type and the application/installation. The module construction determines not only its cost, but also its lifetime. Module design has occupied a significant portion of the development efforts in photovoltaics, and the complexities and details for all photovoltaic materials are beyond the scope of this review. However, module issues are almost as important as cell issues because they directly impact the performance, lifetime, and cost of the photovoltaic technology. Certainly, the importance of module design, features, evaluation, and certification is indicated by the substantial efforts by manufacturers, government laboratories, and other research entities in ensuring this co-dependent component of technology deployment [512–516]. The best, most cost-effective cells would be rendered useless if the module did not adequately provide its required interconnection, protection, and support functions at a low cost. Perhaps one mistake that impeded module development was that early on it was considered primarily from mechanical aspects—just a support for the expensive converters that do the real work of photovoltaics. These components have numerous intimate interfaces among metals, insulators, and semiconductors, energy transfer locations, varying electrical fields, and large surface areas that require micro- as well as macro-area design to meet the demands of operation in varying environmental conditions. The module is more; it is a composite optical and electrical structure that has required the collaboration and overlapping knowledge of physics, chemistry, materials science, and engineering to ensure viability. It is also an evolving area of photovoltaic technology and industry development; one that has to adapt, redesign, and reconfigure with the progress of the various cell approaches discussed previously in this review. The module is central to meeting not only the *efficiency goals* (e.g.

15–25% for modules), but also the *system cost* (e.g. \$1.00–\$1.50/W) and *system lifetime* (e.g. > 30 years) in the 2010–2030 time-frame [30].

Even the most developed and commercialized of the photovoltaics approaches, crystalline Si, has required many redirections of its module make-up to meet either operational or cost limitations over the past 25 years. Two examples highlight this ability and necessity for change. First, the module has been redesigned to eliminate framing to decrease materials cost, and improve loading (weight) and aerodynamics when configured into the array [517]. In this same area, some modules, traditionally only the DC delivery system, have integrated the inverter technology into its construction to meet AC energy requirements [518, 519].

The *second* illustration has been more of a serious one for the technology. That has to do with the encapsulation of the Si cells in a polymer—commonly ethylene-vinyl acetate or EVA [520]. This encapsulant was identified through several development programs as a cost-effective and environment-resistant material for PV modules in the late 1970s. In the mid-1980s, modules deployed at Carrisa Plains, California, were observed to yellow and brown after some 3–6 years of operation in V-trough-mirror configurations to increase the solar flux onto the module surface [521–523]. Consecutive decreases in the annual power output of nearly 10% per year have been documented since 1986. Similar browning of the EVA has also been observed under very specific enhanced UV and heat conditions at other sites [524] and industry laboratories to mitigate the EVA discoloration problem. This has led to a better understanding of the chemistry of the polymer encapsulants used for these applications, and the development of alternative approaches and new formulations to meet the technology needs [525–528]. Examples of the former is the cerium-oxide-doped gas glass superstructure to act as a UV filter for the light before interacting with the polymer and the development of gas-permeable polymer films as superstrates [527–529]. New and improved polymer encapsulants have also been developed to replace the original EVA formulations [527, 530, 531]. These rapid reactions to a potential technology-limiting problems model the ability of the photovoltaic technical community to ensure consumer confidence in its industry's product.

The more recent evolving thin-film and concentrator technologies have additional complexities and likely yet-unknown problems [531–539]. These advanced technologies are very different from their flat-plate silicon ancestors. Consider the thin-film solar cells. Because the surface-to-volume ratios in these cell types are extremely high compared with bulk counterparts, materials and environmental interactions are not only enhanced, but affect relatively larger portions of the structures. These structures are also more complex, beyond the numerous interfaces that are inherent to the device itself (see Figs 17, 19, 21, 34) [532–536]. The cross-sections for a-Si:H integrated module designs, shown in Fig. 44, illustrate areas of concern for shunting (bridges), contact openings, electromigration, interdiffusion, delamination, and microdefects that affect macroscale electrical behavior. Moreover, concentrators present module designs and complexities that have little relationship to their “one sun” relatives [538, 539].

Module design, like cell technologies, have recycled some concepts. In the late 1970s, Si modules had relatively wide spaces between cells to minimize heating effects. Arguments favoring thin-film modules included the fact that module efficiency could be relatively higher because there was no area “wasted” between cells. Silicon module designs evolved with minimal space between the devices. Recently, designs developed having somewhat expanded, reflective intercell areas that redirect the light from those regions back onto the cell surface, increasing the photon flux available for current generation [540]. The reflecting



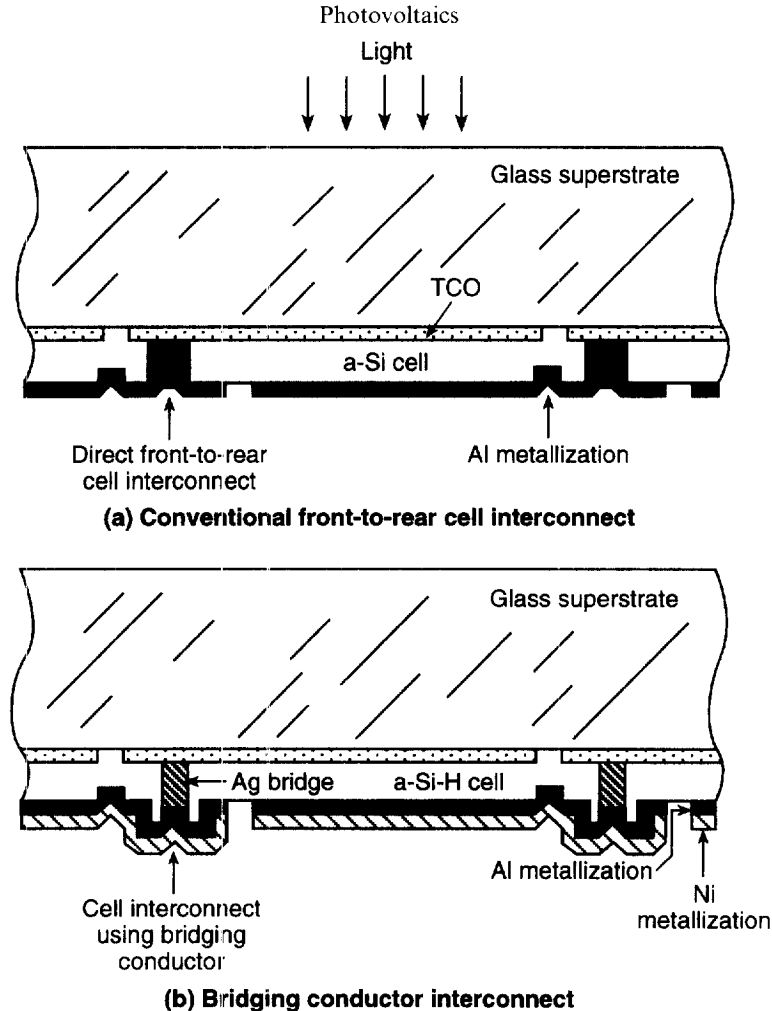


Fig. 44. The cross-sections for a-Si:H integrated module designs illustrate areas of concern for shunting (bridges), contact openings, electromigration, interdiffusion, and delamination.

surface between the cells also helps the modules operate cooler. This and the use of larger cells possibly make the economics of this module design advantageous over the previous generation.

Module performances continue to advance in concert with cell developments. An example is in the amorphous technologies: 5–8 years ago, all amorphous silicon modules had efficiencies in the 3–5% range after extended operation in light. With the advancement of material understanding and cell design, stabilized modules are typically 6–9%, with exceptional examples exceeding 19% [541].

The development of module certification and accreditation criteria and procedures is accelerating the deployment and acceptance of these module technologies [542]. Testing of these components outside and in controlled environments has helped identify problems in module design and extend lifetimes and reliability. The 30-year lifetime goal for photovoltaic modules is still one to be demonstrated, but it is a goal that should be within reach of

photovoltaic engineering efforts. A compendium of validated module performance data for various thin-film technologies is presented in Table 10. These data, which include voltage, current, fill factors, and power ratings, can be compared to the cell parameters in the previous sections of this review to identify some potential areas for improvement in the incorporation of cells into their actual operational units.

## 9. SUMMARY

This brief excursion into photovoltaic cell and module technologies has covered a relatively large number of solar-cell approaches. Again, the paper is not an exhaustive treatment, but it is meant to provide a thorough introduction to state-of-the-art research and development areas. Current cell and module performance represent only a consideration of data available at the time of writing. Photovoltaic advancements are rapid, and these results present but a single frame of a technological motion picture. The choice of “winning” technologies has not been made by any of the photovoltaic programs worldwide. The promise exists for both thin films and single crystals, for flat plate and concentrators, and for silicon and compound semiconductors. However, some of these technologies will be abandoned in the coming period as technology choices are made. However, research is required—not only for the improvement of champion technologies, but also for the generation of new devices and novel approaches. Quality research and good science not only have a place in photovoltaics, but are basic requirements for technology advancement. It must be emphasized that “performance” includes not only energy output and efficiency, but reliability, stability, durability, and a long operating lifetime. The emphasis is sometimes on cell technology, but because of the commercial and consumer aspects, module research and development must continue to receive adequate attention.

Photovoltaics has evolved over the past 30 years from the infancy of a technological curiosity to a commercial enterprise on the brink of incredible growth. Arguments for its deployment can be made on social, philosophical, political, and technical grounds. However, realistically, much R&D remains to be accomplished before the technology can have the expected large impact on the world’s energy generation. This is a challenge, and currently one that remains in the arms of the scientific and engineering community, which must take the lead in providing the understanding, the demonstrations, and the vitality that photovoltaics requires. This technological base—from university laboratories through industry manufacturing lines—must deliver a product that makes photovoltaics the clear and competitive choice of the policy makers, the financial investors, the regulators, and most of all, the users and consumers.

*Acknowledgements*—The author expresses his most sincere gratitude and appreciation to colleagues Richard Ahrenkiel, John Benner, Timothy Coutts, Robert McConnell, Fuad Abulfotuh, Helio Moutinho, Rommel Noufi, Arthur Nozik, Ramesh Dhere, Peter Sheldon, Thomas Surek, Mark Wanlass, and Kenneth Zweibel who selflessly helped in reading, reviewing, revising, and adding to this review. Special thanks go to Keith Emery (whose workload increases substantially every time this author embarks on ventures such as this) for his counsel and sharing his warehouse of knowledge on PV performance and characterization. The author also wants to point out that some of the opinions expressed in this review are based upon his experiences, observations, and thought, and do not represent policy of the National Renewable Energy Laboratory or the U.S. National

Photovoltaics Program. This paper was prepared partially through the support of NREL and the U.S. Department of Energy under contract No. DE-AC36-83CH10093.

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## APPENDIX I

Compendium of reported photovoltaic devices, illustrating the extent of semiconductors and materials investigated for this technology application during the growth years (1972–1981) for terrestrial applications.

This summary covers the growth decade for terrestrial photovoltaics (1972–1981) during which R&D expanded rapidly. Activity was directed toward the development of new materials and a variety of device types. This appendix lists solar cells according to device configuration (i.e. homojunction, heterojunction, Schottky barrier, metal-oxide-semiconductor (MOS), and semiconductor-insulator-semiconductor (SIS)). Parameters including crystallinity (S = single crystal, P = polycrystalline or multicrystalline, R = ribbon, and A = amorphous); bandgap,  $E_g$ ; open-circuit voltage,  $V_{oc}$ ; short-circuit current density,  $J_{sc}$ ; fill factor, FF; conversion efficiency,  $\eta$ ; illumination conditions (either in air mass, AM, or in  $\text{mW/cm}^2$ ); and antireflective coating, ARC. Very few of these cells were verified in a standards laboratory (current standards were not yet adopted), and the efficiencies should be taken as the best possible measurement by that group or that time. This listing is not exhaustive, but is included in this review to give a flavor of the diversity and amount of R&D activity that formed the embryonic years in developing our technology. During this time, many approaches were considered, funded, and evaluated. Many have been abandoned; others have endured to form the commercial basis of the photovoltaics technology. Some of these research devices and materials are currently being resurrected because technology has caught up with the ability to design, process, and measure many of these advanced approaches. In any case, it is interesting the breadth and volume of approaches that were considered in these early stages of terrestrial photovoltaics.

## APPENDIX II

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